STUDY OF DIRECT OXIDATION OF NATURAL GAS TO METHANOL

FINAL REPORT

APRIL 1985

DSS File No. 22ST 23440-4-9011

Cont. Ser. No. OST83-00404

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MICROMEDIA

182 pp

SUMMARY:

The major achievement in this work was the ability to obtain results which indicated a high specificity of methanol ~up to 95%. Conditions were relatively insensitive and ranged from about 20 atm to 65 atm pressure with oxygen from 5 to 10%. The optimum temperature varied from 350° to 450°C depending on the level of C_2 and C_3 hydrocarbon present in the gas. No strong catalytic effects were noted and in one case, 10% Cu on SiO_2, the effect indicated an inertness with results similar to the uncatalysed reaction, i.e. the glass on Teflon lined reactor.

Reaction at as low a pressure as 10 atm and 1 atm is also feasible and but would require a recirculating system. Thus the homogeneous reaction is now capable of being studied by other methods.

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ABSTRACT

This work is a continuation of an ongoing project on "The Direct Conversion of Natural Gas to Methanol by Controlled Oxidation at High Pressures".

The report is divided into six parts. In the first part 100% efficiency of reactant mixing was shown to be essential in the dual flow system and was achieved by incoporating a vernier needle valve to act as a flow constriction and by packing the mixing chamber with Teflon strips. The exit line temperature was restricted to 100°C to prevent the decomposition of product methanol.

The methanol yield improved with increasing pressure particularly when it was raised from 30-50 atm, though less so when increased from 50-65 atm. The optimum methanol yield (86.5% of total oxidized carbon) was achieved at 65 atm at 5% O_2 concentration.

In the second part a comparison between the oxidation of methane and the oxidation of natural gas was made. For methane the most satisfactory operating reaction temperature was determined to be 450°C while for natural gas it was 350°C. Similar yields of methanol were obtained in both cases (80%).

The reduction in operating reaction temperature can be attributed to the presence of ethane and propane in the natural gas which appear to sensitise the reaction. Air was used as the oxidant in place of oxygen for the oxidation of natural gas in Part III.

Although the associated nitrogen did not affect the methanol yields at the lower air concentrations (10.4%); not all of the available oxygen was consumed at the higher levels of air studied (14.8 and 20.6%).

Increasing the diameter of the reactor (to 13 mm I.D.) increased the reactant volume flow rate. The methanol yield improved, over that previously determined in the smaller reactor (4 mm I.D.) by approximately 10% over a glass lined surface, under similar conditions.

The larger diameter reactor allowed the insertion of both catalyst coated tubes and packed catalysts, and a determination of their effect on the oxidation of natural gas. The results obtained in Part IV demonstrate that the reaction is essentially gas phase though the reaction can be inhibited by an "active wall" such as silver or copper at 350°C.

The highest methanol yields (91-92%) were obtained over an inert wall such as glass or teflon.

The heterogeneous catalysts studied were generally overactive resulting in the complete oxidation of the hydrocarbon to carbon dioxide and water. The 10% Cu/SiO_2 catalyst produced methanol in high yield at 357°C and the $Sb-SnO_2$ catalyst exhibited some short term activity at 300°C.

The reduction in the reaction pressure to 10 atm, in the Part V of the report, demonstrated that methanol can be produced in good yield (90%), though at a lower conversion of hydrocarbon (6-7%) since less oxygen can be consumed at these pressures at 350°C.

Further reduction of the reaction pressure to atmospheric was offset by the increase in reaction temperature necessary to initiate the reaction (440°C).

It was demonstrated that the reaction can be run continuously using a Recirculation System which allowed the recycling of unconverted natural gas.

The recycle system provided for collection of the product methanol and water and the removal of carbon monoxide and carbon dioxide. The residual gas consisting of methane, ethane and propane was repressurized, remixed with oxygen and reintroduced into the reactor.

The Recirculator was found to operate successfully and demonstrated the potential of a recycle system. The summary of an economic study is given in Part VI. This study showed that a small plant processing 1 million cubic feet (28.3×10^6 litres) of natural gas a day can yield methanol at a cost of from 11.5 to 18.5 cents/liter (45 to 70 cents/U.S. gal). This compares favorably with production costs from larger plants.

EXECUTIVE SUMMARY

This project is a continuation of last year's work dealing with the direct conversion of methane (CH_4) to methanol by oxidation at high pressure.

The most widely used method at present to convert methane to methanol, involves the following two separate reactions:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1)$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (2)$$

The excess hydrogen (H_2) in reaction (1) is used to produce heat or more CO is added to consume it.

It seems wasteful of energy and resources to first break all carbon-hydrogen (C-H) bonds in methane (CH_4) and then to reform three of these bonds in methanol (CH_3OH). Thus, this project was devoted to the study of the direct oxidation reaction

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3OH$$

In the previous year we were able to improve upon the yield of methanol obtained (i.e., 80% based on consumed methane which represented 10% of the input methane gas at pressures of 50 atm) over that obtained by other workers (65% methanol yield based on 5% consumed (184 atm methane) at 450°C.

In the work carried out in the present contract the oxidation of natural gas was studied where yields of methanol in excess of 80% based on consumed hydrocarbons were obtained at a lower operating temperature of 350°C at 10-65 atm. Yields of this order were obtained irrespective of whether air or oxygen was used as oxidant, at 50atm.

The reaction was found to be essentially gas phase with the five bulk catalysts studied having little, if any, effect on the reaction.

The nature of the wall did influence the reaction and the reaction proceeded optimally over an inert wall such as glass on Teflon.

Recirculation of the unconsumed reactant gas through the reactor increases the amount of natural gas converted, in a closed recycle system. Such a system proved reliable in operation and permitted the collection of the condensable reaction products which included methanol. An economic summary and evaluation of the process is presented which was based on the experimental data and gave production cost (45 cents to 70 cents/U.S. gal) which compared favorably with the methanol price from the larger plants used at present.

Ce projet, dans lequel la transformation du gaz naturel en méthanol est effectuée par oxydation (à pression élevée), est une suite logique du travail effectué l'année dernière.

De nos jours, la méthode la plus répandue pour convertir le méthane en méthanol, implique les deux réactions suivantes:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1)$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (2)$$

L'excès d'hydrogène dans la réaction (1) est utilisé pour produire de l'énergie, sinon plus de monoxide de carbone est ajouté. Il ne semble pas rentable, en énergié et ressources, de briser tous les liens carbone-hydrogène (C-H) du méthane (CH_4), pour ensuite reformer trois de ces liens dans le méthanol (CH_3OH). Donc, le projet était d'étudier la reaction suivante:

$$CH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_3OH$$

L'année dernière, nous avons été capable d'améliorer la production de méthanol (80%; basé sur la consommation de méthane, lequel représentait environ 10% du méthane utilisé, à 50 atm) en comparaison avec les résultats obtenus par d'autres chercheurs (rendement de 65% en méthanol, basé sur la consommation du méthane, lequel représentait environ 5% du méthane utilisé) à 450°C.

Dans le travail fait pour le présent contrat, l'oxydation du gaz naturel a été étudiée, et des rendements supérieurs à 80% en méthanol,

basé sur la quantité d'hydrocarbone consumée, ont été obtenus à une température plus basse (350°C) et à 10-65 atm. Des rendements de cet ordre ont été obtenus aussi bien avec l'utilisation de l'air ou de l'oxygène, à 50 atm.

La réaction était essentiellement dans d'état gazeux avec la majeure partie des catalyseurs étudiés (seulement 5 ont été examinés) ayant très peu d'effet sur la réaction. Cependant, l'intérieur du réacteur a influencé la réaction, laquelle donna les meilleurs résultats lorsque l'intérieur du réacteur était en verre ou en Teflon.

La recirculation du gaz non-consommé à travers le réacteur, dans un système fermé augumente la quantité de gaz transformé. Un tel système a été démontré comme étant efficace et permet l'échantillonnage des produits de la réaction, incluant le méthanol.

Un compte rendu économique et une évaluation du procedé sont présentés. Ce rapport est basé sur les faits experimentaux, et donne un coût de production de $0.45-0.70/gallon US, lequel se compare favorablement avec ceux obtenus dans l'industrie.

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INTRODUCTION:

This report is a summary of work continuing from the previous contract "The Production of Methanol by the Controlled Oxidation of Methane at High Pressures", DSS File No. 20SU23440-2-9106, Serial No. 0SU82-00266, submitted in May 1984.

The objectives of this contract were to complete the work not completed in the previous contract and to perform the following tasks:

1. Reactor Modification: To construct and test a recycling system whereby the unreacted CH_4 would be returned to the reactor and recycled and the products (H_2O and CH_3OH) removed by cooling and (CO and CO_2) removed by reaction.
2. Direct Oxidation of Natural Gas: To establish reaction parameters for Natural Gas as compared to pure methane, and to characterize the effects of higher hydrocarbons such as ethane and propane on the oxidation reaction and yields of methanol.
3. Catalytic Effects: To determine the effects of various catalysts on the yields of methanol and the conversion of methane as well as the effect on the reaction parameters.
4. Oxidation Runs with Air: To study the effect of air as the reactant as compared to pure oxygen.
5. Process Economics: To economically evaluate the process in terms of the product yields and conversion obtained.

All these tasks have been performed.

This project has tremendous potential in terms of its relevance to the Canadian economy. The world wide surplus of Natural gas and the concommitant shortage of liquid (storageable) fuel makes the conversion of Natural gas to methanol and subsequently to gasoline an attractive process which is presently being introduced in New Zealand. At recent conferences (1,2) where the results of this project were presented great interest was stimulated and it is obvious that we are at present ahead of everyone in what is believed to be the logical process of converting Natural gas into a storageable fuel. Our review of the literature has been accepted by Chemical Reviews in the revised form and will be appearing shortly (3).

Our results indicate that reasonably high yields of methanol can be obtained at the low pressure of 10 atms. Hence we believe that it should be possible to convert part of the Natural gas into methanol as it leaves the well head and before it enters the pipeline. This could mean that a vehicle fuel may be available in isolated northern communities in Canada as Arctic Gas becomes available.

This report is divided into 6 parts as follows:

1) Effect of temperature (455° to 515°C) and pressure (35 to 65 atm) on the oxidation of CH_4 with O_2.
2) Oxidation of Natural Gas with oxygen.
3) The oxidation of Natural Gas with air and the reaction in a glass lined reactor.
4) Catalytic studies.
5) The oxidation of Natural Gas at Low Pressures and the Recycle system.
6) Economics study of reaction process.

PART I. THE EFFECT OF TEMPERATURE AND PRESSURE ON THE OXIDATION OF METHANE BY OXYGEN

INTRODUCTION

This part sets out further results in the study of the controlled oxidation of methane using the dual flow reactor. It covers four areas: (i) Refinements to the dual flow system to obtain reproducible yields comparable to those obtained using the monoflow system, (ii) Systematic study of the reaction at 35, 50 and 65 atm at various oxygen levels, (iii) Improvements made to the detection system (G.C.), and (iv) Effect of temperature on the oxidation of methane.

EXPERIMENTAL PROCEDURE

Mixing of Reactants

Achieving thorough mixing of the reactant gases appeared to be the main obstacle in obtaining methanol in good yield as discussed previously (4). Evidently there was insufficient turbulence occurring in the mixing cross and so two modifications were made.

1. Porous polyethylene discs were cut and placed in the brass fittings which immediately followed the check valves which admitted CH_4 and O_2 respectively into the mixing cross. The mixing cross itself was filled with Teflon turnings to reduce the dead volume and again improve turbulence.

2. A vernier needle valve (Aerosmith V54-2-11) was inserted into the input line following the mixing cross. A study was conducted wherein the reactant mixture composition (O_2 and CH_4) was determined immediately after passing through the needle valve at the missing cross, via a sampling loop, and this was compared with the mixture after it had passed completely through the system, i.e. at the gas sampling valve (GSV), for various settings of the vernier. The optimum setting was found to be with the vernier turned one 360° turn out from fully closed. This produced a mixture at the GSV which contained no more than 116% of the O_2 in the CH_4 mixture at the mixing cross. In practice this value approached 100% and indicated complete mixing of the reactants before the reactor after the throttle valve.

These measures increased the degree of mixing to give a practically homogeneous mixture. The effect of this in terms of methanol yields are discussed below.

Exit line temperature

The exit capillary line temperature was investigated at various points along its length up to the GSV. The temperature was found to increase quite markedly around the GSV sampling loops. The temperature for the majority of the line was between 180-200°C which agreed with the two thermocouples which were used to monitor the temperature during the course of an experimental run. The temperature at the GSV, however, was close to 300°C and this was presumably caused by the more tightly wrapped lagging around the sample loops, i.e. the heat loss at this point was much less than that along the remainder of the line. The temperature of the exit line was reduced and subsequently increased during the course of an experimental run to check if this affected the product and in particular the methanol yield.

Experimental runs

A total of 11 experimental runs were made. Run 23 allowed for a determination of the effect that the degree of mixing had on the yields. The experimental procedure involved setting the reactant composition, at room temperature and at the chosen pressure, to within 1% of the desired O_2 in CH_4 value. The reactor was then "speed heated" to 450°C, held constant, and the products analysed. Runs 24-26 were conducted at 50 atm at 6.7, 3.5 and 8.0% O_2 respectively. Runs 27-29 were conducted at 35 atm and at 2.1, 6.0 and 10.3% O_2 respectively. Runs 30-32 were carried out at 65 atm. Here each determination of the experimental yield was made at two heated reactor zone lengths of 35 and 45 cm. Run 30 was performed at 2.6% O_2, run 31 at 5.15% and run 32 at 7.3% O_2.

In Run 33 the effect of temperature on the oxidation of methane was investigated at 455°, 461°, 477°, 483°, 510° and 515°C at 65 atm and 4.74 % O_2.

Evaluation of alternative G.C. packings and procedure

Porapak S packed in a 10'(305 cm) x 1/8"(0.32 cm) o.d. SS column, though very satisfactory for the separation of the reaction products, showed a tendency to retain water and to a lesser extent methanol on analysis. Although these amounts were reasonably small (10% H_2O) they would nevertheless build up on the column and their transfer during subsequent elution could not be ignored.

In an effort to improve this situation several column packings were investigated which were thought to be suitable for analyses involving water and which also permit single column resolution of all the reaction products. These packings included Porapak Q (Waters Associates), Chromosorb 102 (Supelco Inc.) and Carbosieve B (Supelco Inc.) in 10'(305 cm) x 1/8"(0.32 cm) o.d. SS columns and Porapak S additionally packed into a 10'(305 cm) x 1/8"(0.32 cm) o.d. Teflon column.

RESULTS AND DISCUSSION

Mixing of Reactants

A comparison of the inlet and outlet (to the reactor) composition of the reactant gas mixture (O_2 in CH_4-N_2; N_2 in CH_4 2%) at various settings of the vernier valve was made and the degree of mixing determined at 50 atm and room temperature (Table 1). Once the optimum setting of the valve was established, the reactor temperature was raised to 450°C and the reaction products analysed (Table 2).

These results show a clear improvement in yield with respect to methanol, compared to those obtained previously (see Tables (6a) and (6b) in 1984 Final Report,Run #21b), of around 25% compared to the situation of no vernier valve but steel wool only.

The average yield for the reaction, at O_2 concentrations between 5-10%, in the case of no mixing at all (empty mixing cross) was 8.5% for methanol. With steel wool in the mixing cross, at 10% O_2, this figure rose to 33.6% and with insertion of the vernier valve (and replacement of the steel wool with Teflon turnings) and polythene porous discs the yield increased to 57% (at 7% O_2). This latter figure compared well with the yields obtained using the monoflow system (see Tables 1A and 3A, Appendix A, 1984 Final Report).

Exit line temperature

The effect of the exit line temperature, particularly at the GSV, on CH_3OH yield was evaluated during an experimental run (Table 3(a) and (b)). These yields can be directly compared with those obtained during the run when the exit line heater was switched off (Table 3a).

Not heating the exit line (capillary section + GSV) improved the yield of CH_3OH by 20% (i.e. from 60% to 80%).

Overall good mixing accounted for an increase in CH_3OH yield from 8.5 to 57% and non-heating of the exit line, i.e. line insulated without external heating improved the yield further to 80%.

The combination of the polythene discs in the CH_4 and O_2 entrances to the mixing cross, the Teflon turnings packed in the cross and the vernier valve constricting the flow immediately following the cross had presumably caused turbulence in the gas stream, breaking up the laminar flow, and effecting interdispersion of the relatively smaller O_2 stream in CH_4.

The effect of reducing the exit line temperature, particularly at the GSV, indicated that some decomposition of the CH_3OH was taking place either in the gas phase or on the stainless steel walls of the tubing. It would be interesting to study the fate of CH_3OH at the reaction temperatures and pressures presently used since it is not known if the CO and CO_2 form from CH_3OH or directly from CH_4.

Reaction analysis

All results of reaction analyses represent values obtained once a steady state situation in the reactor had been reached unless otherwise stated. The results have been tabulated in Tables 2-12. These Tables include figures for the carbon balance, percent CH_4 converted, and the percent methanol yield from reactant CH_4.

The results are presented in two ways: 1. The variation in yield of the oxidised product as a percentage of the total oxidised product as a function of inlet $\%O_2$ concentration, and 2. The variation in the percentage yield of CH_3OH converted from methane, i.e. the product of the (% oxidised product yield) x (percentage conversion of CH_4). This value of course should compare with the yield of CH_3OH as a percentage of the total carbon product (see Tables 3-11).

At 35 and 50 atm these values agree fairly well, however, at 65 atm the agreement is a little less satisfactory and this is reflected in the carbon balance where the value of the output/input carbon rises to 121% as opposed to above 90% for determinations made at 35 and 50 atm. Both of these discrepancies occur due to the higher yields (particularly of CH_3OH) of oxidised carbon product which occur at higher pressures and particularly at higher O_2 concentration. This can be attributed to the difference in sensitivity which the Kromo-Tog thermal conductivity detector had, between methanol and water on the one hand and the gaseous components of N_2, CO, CH_4 and CO_2 on the other. Since helium is used as the carrier gas it was always assumed that the difference between the respective thermal conductivities of the products was small relative to Helium. Indeed it has been shown that the detector is slightly less sensitive to CH_4 than CH_3OH by a factor of 0.97 at the same amplifier attenuation (Appendix 1A). The sensitivity to the permanent gases is comparable to that of CH_4. The detector is less sensitive to H_2O compared to CH_3OH by a factor of 0.65. The linearity of the amplifier with respect to N_2, CO, CO_2 and CH_4 was good at various attenuation settings but not quite so good for CH_3OH (Figures (i), (ii), (iii) Appendix 1A). It would be expected therefore that the methanol yield would be subject to some error in this respect and that this would be included in the carbon balance. If the relative sensitivity of CH_4/CH_3OH is taken into account then the values for the methanol yield as a percentage of the total carbon in the products, and that obtained from the (degree of conversion) x (% yield CH_3OH of oxidized carbon product), agree within the range of the respective standard deviation. This correction is shown in one set of determination (Table 11(b), see Appendix 1B).

The results show that the highest average yield of CH_3OH as a percentage of the total oxidised carbon product using a 45 cm heated reactor zone was 86.5% at 65 atm, 450°C at an O_2 concentration of 5.15%. This value represented a maximum at 65 atm (Figure 1). At 50 atm the yield was above 80% except at the highest O_2 concentration of 8.0% while at 35 atm the yield decreased almost linearly as a function of increasing O_2 concentration suggesting the reaction was under kinetic control (Figure 1). Figure 4 shows that the largest percentage of CH_4 converted to CH_3OH was 22% at 65 atm 450°C at just under 7.5% O_2. Interestingly the amount of CH_4 converted maximized at 6.7% O_2 at 50 atm. At 35 atm the amount of CH_3OH increased again linearly with increasing $\%O_2$ concentration.

All the above results were obtained using a 45 cm heated reactor zone (Tables 3-8). At 65 atm alone determinations were made at both 45 and 35 cm heated reactor zone lengths (Tables 9-11). For the 35 cm heated zone the yield of CH_3OH was increased slightly throughout the range of O_2 concentration studied, though the increase was more pronounced at the lowest % O_2 value (Tables 9(a) and 9(b)).

In Figure 5 the variation of these methanol yields and methane consumption with reaction temperature are shown at an oxygen concentration of 4.75%. The general tendency is for the methanol yield to increase slightly with temperature before levelling off. It was expected that the yield would maximize at some point, as the oxidation rate increases, though this was not sharply observed it can be seen that the yield reached a plateau at 480-510°C with a slight decrease at 515°C. The highest yield of CH_3OH recorded was 85% at 510°C. The yields of carbon monoxide and carbon dioxide varied inversely with the methanol yields, again as the oxidation rate increased it would be expected that their yields would increase. As with methanol these yields did level off at 480-510°C before rising slightly (Table 12(i)-(vi)).

In all these results most, if not all, of the O_2 was consumed and it is obvious that a higher conversion would be achieved if more oxygen were added to the reactant. However, the uncertainty in the explosion limits makes further increase in oxygen concentration unsafe.

Evaluation of Column Packings

Of all the column packings investigated Porapak Q and Chromosorb 102 emerged as the ones which gave the best separation/resolution of the reaction products of interest and in particular in distinguishing the formed reaction products from the constituents of natural gas. These packings allow for good separation of air, CO, CH_4, CO_2, C_2H_6, H_2O, C_3H_8, $(CH_3)_2O$ and CH_3OH (see Table 13). Porapak S, while permitting the separation of air and CO, would not separate C_3H_8 from H_2O.

The problem of water retention by this packing was reduced by treating it with hexamethyldisilazane. Though Chromosorb 102 offered good resolution of the same compounds as Porapak Q its peak to peak separations were inferior.

Carbosieve B separated O_2, N_2, CO and CH_4 well but would not separate H_2O from CH_3OH.

In conclusion, it would seem that the best system would be a combination of Carbosieve B or a molecular sieve in one column and Porapak Q in another to permit a dual column analysis that would involve backflushing compounds with boiling points higher than CH_4 and CO_2 onto the Porapak Q column for temperature programmed elution for which a suitable GSV will be required.

Another possibility with regard to the above separations is the operation of a suitable packing at cryogenic temperatures to effect the separation of O_2, N_2 and CO with subsequent temperature programming to permit the separation of the higher boiling compounds. Such an operation would permit the use of a single column. Accordingly a Porapak S in Teflon (10'(305 cm) x 1/8"(0.32 cm) o.d.) column was packed and tested in this manner. The Teflon tubing made the column flexible enough to be lowered into a slush bath (-78°C). Separation of O_2, N_2 and CO was good but the column was not very efficient in separating CH_3OH, H_2O and $(CH_3)_2O$, with these compounds appearing as broad peaks incompletely separated. It can only be assumed that the Teflon tubing was effecting positive adsorption of these compounds at the final temperature of the program (180°C).

It is intended to test this application again using Porapak Q or Chromosorb 102 as the packing which give the desired separations at lower final temperatures, 125 and 75°C respectively.

CONCLUSION

The measures taken to improve mixing of the reactants in the dual flow system proved effective in achieving 100% mixing. Evidently a certain degree of turbulence at the mixing point was necessary to achieve this, and this immediately benefitted the methanol yield.

It was discovered that methanol could be quite easily decomposed (CO_2 + H_2O) by contact with a hot steel surface (200°C) and careful monitoring of the exit line and GSV temperature prevented this and ensured the preservation of the maximum yield of methanol.

There would seem to be little advantage in increasing the reaction pressure above 50 atm as the yields of methanol and the amount of reacted methane improved only slightly at 65 atm at the oxygen concentrations studied (10%).

Although a sharp value for the optimum temperature, for the oxidation of methane, in terms of methanol yield was not obvious, it was evident that the yield did not benefit much by operating at temperatures above 480°C. Indeed at the higher temperatures the increased oxidation rate favored CO and CO_2, probably emanating from the decomposition of methanol.

The reaction would consume more oxygen even at 35 atm if its concentration were to be increased though the safety limits for this are not known. There was some evidence that a reduction in reactor volume improved the methanol yield.

PART II. OXIDATION OF NATURAL GAS WITH OXYGEN

INTRODUCTION

Outlined in this part are the results obtained from studies of the oxidation of natural gas with oxygen. Use of natural gas complicated the product chromatogram and the necessary procedure modification is discussed.

EXPERIMENTAL PROCEDURE

In this part, five experimental runs were carried out. Runs 34-36 involved a study of the oxidation of natural gas at various temperatures at 65 atm and runs 37 and 38 at 50 and 35 atm, respectively, at 350°C. The oxygen concentration in all of these runs was kept around 5% or less of the total reactant.

In an effort to improve the analysis of natural gas and its reaction products Porapak T was packed into a 10'(305 cm) x 1/8"(0.32 cm) o.d. stainless steel column. It was thought that the higher polarity of this packing compared to Porapak Q would facilitate the separation of air from CO at room temperature, which was not possible on Porapak Q. It was also hoped that this increase in polarity would improve the separation of propane from methanol compared to that obtained using Porapak Q and permit the separation of any other possible products such as dimethyl ether and ethanol. However, as with Porapak S it was likely that a column this polar would retain water to a certain extent.

The steel columns used in these investigations were coiled such that they could be inserted into a Dewar and thus allow sub-ambient operation of the packings, so that O_2 and N_2 could be separated. Porapak Q was found to be the more efficient packing in this regard and at -78°C nitrogen could be separated from oxygen with good resolution. This procedure was necessitated by the sometimes incomplete consumption of reactant oxygen in the natural gas studies, owing to the lower reaction temperatures employed (discussed below). This procedure was also useful in determining the concentration of the internal standard, nitrogen.

In the natural gas studies, a gas obtained from fields in Tennessee was selected on the basis of its ethane and propane content (Matheson Gas Products) at 4.5 and 2% (Table 14), respectively, which was considerably higher than that found in domestic supplies (Trans Canada Gas) as most of the higher hydrocarbons are removed for other purposes. The Tennessee natural gas (TN-Ngas) contained nitrogen at a level of about 0.45% of the methane content and this was considered an adequate amount to act as an internal standard.

Initially, in experimentation with TN-Ngas an attempt was made to remove the CO_2 contained therein using BaO and Ascarite (NaOH on asbestos). BaO, however, proved less than effective and while Ascarite removed CO_2 completely it tended to lose its efficiency over a period of time thus complicating the oxidation studies. This was most probably due to insufficient Ascarite being used (packed into a 35cm x 0.85 cm i.d. stainless steel tube). It was more convenient to leave the CO_2 in the reaction gas stream at a known concentration and monitor the total CO_2 in the product analysis.

RESULTS AND DISCUSSION

Oxidation of Natural Gas

The results obtained from runs 34-38 have been tabulated in Tables 16-19, and are represented in graph form in Figures 6-7. Included in these figures is the variation of the percent methanol, carbon monoxide and carbon dioxide as yields of the total oxidized carbon product, the percent methane or hydrocarbon (TN-Ngas) consumed and the percent methanol converted from methane/hydrocarbon and residual oxygen.

As mentioned previously TN-Ngas was selected as the most suitable natural gas to be studied. Its composition was determined prior to every run to monitor its integrity and a general analysis is given in Table 14.

It was anticipated that use of natural gas would effect a reduction in the reaction temperature. Runs 34-36 set out to determine the effect of temperature on the reaction (Figure 6).

The results, at 65 atm, show that the highest yield of methanol, 95%, was obtained at 310°C at 3.8% oxygen concentration. The amount of hydrocarbon consumed was small, however, at 7.5%, and the yield of methanol converted 7%. At low temperatures the oxidized product was predominantly methanol and only around one quarter of the reactant oxygen (included in figure) was consumed suggesting that the oxidation rate was low. Carbon monoxide was not detected (by G.C. analysis) in any of the determinations at this level. Evidently the low rate of oxidation favoured the methanol yield, i.e. in a limited reaction at 65 atm.

As the reaction temperature was increased the reaction rate increased and consequently the oxygen consumption. The oxygen content of the reactant mixture was increased to 5.5%, and the results at 360° and 368° show that the bulk of the reactant oxygen was consumed. Yields of methanol were reduced as the yields of CO_2 increased, and CO was now formed.

At 410°-428°C the yield of methanol began to level off albeit at a higher oxygen concentration.

Neither the amount of hydrocarbon consumed nor the percent methanol converted increased significantly in going from 360° to 430°C.

In summary, the yield and consumption values obtained using natural gas at 360°C and 65 atm were comparable to those determined at 460°C at the same pressure using methane (Figure 1, and Figure 4) at the 5% oxygen level.

As previous workers had found, substitution of natural gas, with moderate ethane and propane content, for methane afforded about a 100°C reduction in reaction temperature giving comparable yields. In agreement with previous work the total oxidized yield could not be accounted for simply in terms of the depletion of ethane and propane (levels of higher hydrocarbons in natural gas remained constant in this study) see Table 15. As can be seen, based on the carbon balance, 95% of the oxidized carbon is derived from the methane in the natural gas. It would seem that the ethane and propane, though consumed in relatively smaller amounts, exert a considerable activating influence on methane.

The effect of pressure on the oxidation of natural gas was investigated at 35, 50 and 65 atm (Figure 7).

Although at 65 atm the oxygen concentration was 5.5%, the general indication was that the percentage yields of methanol and methanol converted began to level off/decrease above 50 atm. At 50 atm all of the oxygen is consumed whereas at 35 atm, at a similar oxygen concentration, about 40% of the oxygen available was consumed. At 65 atm a greater amount of oxygen is consumed with a little left over and this is reflected both in the amount of hydrocarbon converted to methanol and the carbon dioxide and monoxide yields.

In summary of the pressure results, it would seem that methanol can be selectively obtained in moderate yield at 50 atm and 350°C from the oxidation of natural gas using oxygen levels below 5%.

ANALYSIS

Porapak T (50/100) in a 10'(305 cm) x 1/8"(0.32 cm) o.d. stainless steel column was used almost exclusively for the analysis of the reaction products in the studies of the oxidation of natural gas. The use of this packing allowed good separation and resolution of all the components of natural gas of interest (up to C_4) and of the major reaction products. The high polarity of the packing relative to Porapak Q meant that some retention of the polar reaction products, particularly water, was a problem. Treatment of the column with HMDS (hexamethyldisilazane) and acetone (as suggested by Alltech Associates catalogue) separately, provided limited solutions to the problem. The situation was monitored, by determining the water/methanol ratio independently on Porapak Q, and adjustment made as necessary.

At 4°C Porapak T allowed a reasonable separation of air and carbon monoxide. As mentioned in the experimental procedure Porapak Q at -78°C effected a good separation of oxygen from nitrogen when required.

The analysis would be greatly facilitated by the use of a two column system with a suitable sampling valve.

CONCLUSION

Use of Natural gas in place of methane effected a substantial reduction in the operating reaction temperature, from 450 to 350°C. Although there was reasonable reaction at temperatures as low as 310°C not all of the available oxygen was consumed.

As with pure methane, however, increasing the reaction pressure above 50 atm afforded little improvement in terms of methanol yield though the extent of oxidation was increased by virtue of increased consumption of oxygen.

PART III. THE OXIDATION OF NATURAL GAS WITH AIR AND THE REACTION IN GLASS LINED REACTOR

INTRODUCTION

In this part, a total of 5 experimental runs were completed. The work carried out can be classified into two categories:

(i) The oxidation of natural gas using air as the oxidant in place of oxygen,

(ii) Study of the oxidation of natural gas with oxygen in the large diameter-glass lined reactor [catalytic reactor].

EXPERIMENTAL PROCEDURE

Oxidation of Natural Gas with Air: Runs 39-41

The study of the oxidation of TN-Ngas with air was carried out at a pressure of 50 atm and 350°C at three air concentration levels of 10, 15 and 20% respectively. The experiment at the 15% level was conducted independently at two heated reaction zones of 35 and 45 cm. The flow rate was kept at around 10s/reaction volume. The composition of the reactant air (medical grade) was determined once while that of the TN-Ngas was determined prior to each experimental run (Tables 20 and 21). This experiment was designed to determine if air (a cheaper and more easily obtained oxidant) could be used in place of oxygen and the effect, if any, that the higher associated levels of nitrogen might have on the product yields.

Large Glass Lined Reactor:

A larger diameter reactor was required to accommodate the metal coated glass catalyst tubes and the packed catalyst tubes for the catalytic study.

A suitable length of high pressure stainless steel tubing was obtained (Autoclave Engineers). The ends of the tubing were tapped to accept suitable connections so that it could be adapted into the existing system. An innovation here was the application of a "quick-connect" connector at the input end of the reactor tube which would permit easier dismantling of the reactor to effect the changing of catalyst tubes and improve turnaround times.

The reactor had an inside diameter of 1.43 cm into which a glass tube (1.41 cm o.d. x 1.05 cm i.d., mp = 560°C) was inserted to form a close fit. The inner walls of the glass tube could be coated with metal or the tube could be simply packed with solid catalyst. The internal diameter of the glass tubes, of 1.05 cm, was equivalent to a reaction volume of 39 ml, equal to almost a seven fold increase in reaction volume compared to the previously used stainless steel reactor.

In order to keep the residence time of the reaction mixture constant at 10s/reaction volume (to remain comparable with that used with the smaller reactor)., the increase in reaction volume necessitated that the flow rate, at NTP, be increased to 234 ml/min. This meant a much higher consumption of reactants particularly of the TN-Ngas.

RESULTS AND DISCUSSION

Oxidation of Natural Gas with Air:

The variation of methanol yield and consumption of hydrocarbon with air concentration is shown in Figure 8. The methanol yield depends quite clearly on the concentration of air, decreasing as the level of air increases. Comparison of these yields with those obtained previously (Figures 6 and 7) show that they are directly comparable. It can be concluded, from this comparison, that at the levels of air investigated, N_2 does not interfere with the methanol yield or conversion of Ngas and that the oxygen concentration is the dominant factor (Tables 22-24).

In Run 41b the effect of reducing the heated reaction zone from 45 to 35 cm was studied. The air concentration was 14.8%, the same as had been used for the 45 cm zone, yet the yield of CH_3OH increased by 7% over that obtained at the 45 cm length, although less oxygen was consumed (Table 23). This may have been a carryover effect. Comparison of the % concentration of oxygen consumed (Figure 8, Tables 22, 23 and 24) shows that not all of the available oxygen was used except at the lowest level of air studied (Table 22).

The composition of the reactant air used in these investigations was determined (Table 21). The air in these experiments came from a high pressure cylinder of Medical Air, supplied by Union Carbide. Its composition compared with that of atmospheric air eliminating the possibility of an oxygen rich air source.

The use of such relatively high nitrogen concentrations, in these experiments, which in turn was used as the internal standard, meant that the C/N_2 and O_2/N_2 ratios determined were subject to somewhat larger errors than usual, and consequently the values of % Ngas consumed and % CH_3OH converted are also subject to larger errors than usual.

Large Glass Lined Reactor

Operation of the glass lined large diameter (catalytic reactor) at 50 atm and 350°C resulted in higher than normal yields of methanol and seemingly improved conversion of hydrocarbon. All of the reactant oxygen was consumed (Table 25).

Another run was carried out at a reduced pressure of 30 atm. The methanol yield remained high and the conversion of hydrocarbon returned to the more usual levels (Table 26, Table 19). Mixing of the reactants was determined to be 98.0% efficient.

The carbon balance was high and it may be that the sensitivity of the detector towards methanol, at these higher concentrations, may have changed.

Water was also produced in somewhat larger than usual quantities.

Evidently the increased reactor volume favoured oxidation of the Ngas to methanol allowing a reduction in operating pressure of 20 atm to the 30 atm level giving comparable results to those obtained using the small diameter reactor (4 mm) at 50 atm (see Table 3a).

CONCLUSION

The use of air in place of pure oxygen demonstrated that, at the levels investigated, up to 20% air, that the nitrogen concentration did not have any significant negative effects on the methanol yield although at the higher air concentrations not all of the available oxygen was consumed.

The conversion of natural gas in the larger diameter glass lined (catalytic) reactor was good and the yield of methanol exceeded that obtained in the previously used smaller diameter reactor by some 10% at the 5% O_2 level. This improved the percent methanol converted or methanol specific yield considerably (compare Tables 25 and 16b).

PART IV. CATALYTIC STUDIES

INTRODUCTION

The studies with catalysts required the use of a larger diameter tube in order to facilitate the study of wall effects. This was done by using Pyrex glass tubes as a replaceable liner for the stainless steel. Thus, a coated glass or a catalyst packed tube could rapidly be replaced.

Previous work indicated that copper and silver were effective catalysts (6). Some catalysts samples were also obtained from United Catalyst Inc., (Louisville, KY). Other work in the laboratory on amorphous semiconductors enabled us to prepare and test Aerogels of TiO_2 and SnO_2 doped with Sb_2O_3. Another commercial catalyst "Hopcalite" (Co_3O_4) was also available for testing.

EXPERIMENTAL

In order to facilitate the introduction and removal of catalyst the reactor was lined with a Pyrex glass liner which could be readily removed and interchanged with another. The inside walls of the liner could be coated with metal and wall effects studied. Alternately the tube could be filled with porous catalytic material and the bulk effect determined.

A total of 10 experimental runs were carried out, 5 of which investigated wall effects and 5 the effect of bulk catalysts on the oxidation of TN-Ngas.

In Run 44 a metal coating of silver was deposited on the inside of a glass liner over a length of 40 cm, using the well known Tollen's reaction. The prepared tube was inserted into the reactor. The silver wall was preoxidized in a stream of air, overnight, at 180°C. The reaction was investigated at temperatures of 350° and 400°C at 30 atm pressure and an 0_2 concentration of 5.5%.

In Run 45 the silver walled catalyst tube was replaced by a 1.27 cm (½ inch) o.d. x 60 cm length of copper tubing which was flared at both ends to make a reasonably close fit within the reactor. (An attempt to coat copper onto the inside wall of the glass tubing did not give a continuous film (5)). As in Run 44 the reaction was investigated at 350° and 400°C at 30 atm pressure and an oxygen concentration of 4.73%.

In Runs 46-49 and 51, a glass liner was packed, to 10 cm of its length with the chosen catalyst in such a way that the catalytic section (front of tube) would be heated by the 10 cm furnace which preceeded the 35 cm furnace (kept at 300°C). In this way the catalyst temperature could be controlled independantly.

In Run 46 10% Cu on silica (5 mm spheres) was studied at 350°C and 300°C at an oxygen concentration of 3.9%. In run 47, 10% $Co/\gamma Al_20_3$ (5 mm x 3 mm tablets) was studied at catalyst temperatures between 300 and 350°C at an oxygen concentration of 4.8%.

Hopcalite was investigated in Run 48 at catalyst temperatures ranging from 300°C to 210°C at 5.5% oxygen concentration. Run 49 studied the effect of $Ti0_2$ aerogels at an oxygen level of 4% at catalyst temperatures ranging from 300° to 407°C.

Run 50 was designed to study the oxidation of natural gas at 350°C with an 'inert' surface taking the place of the glass tube. Teflon tubing was chosen for this purpose and a tube with an inside diameter of

0.9 cm was inserted into the reactor corresponding to a heated reaction volume of 28.6 ml. This procedure would help determined the effect, if any, of the glass wall on the reaction.

Some antimony doped tin oxide (a porous glass) was prepared by a sequential reagent addition - centrifugation - precipitation method and packed into a 10 cm length of a glass tube before being inserted into the reactor, to determine its activity with respect to the Ngas oxidation, in Run 51.

The final surface to be studied was that of the stainless steel reactor, i.e. the glass liner was removed and the reaction studied in the presence of the steel walls, at two temperatures (350° and 379°C) (Runs 52 and 53). Removal of the glass liner from the steel tube increased the reaction volume from 39 ml to 72 ml. Maintaining the previously used flow rate (200 ml/min NTP) would cause a substantial increase in the space time and hence an increase in residence time. It was anticipated that this would only influence the extent, and not limit, the oxidation reaction.

RESULTS AND DISCUSSION

The use of silver as a "wall catalyst" had some interesting effects on the course of the reaction (Run 44). As the reaction analysis proceeded with time, the degree of hydrocarbon conversion increased concomitantly with consumption of oxygen, i.e. there was a considerable induction period before the reaction reached a steady state (Table 27).

In the initial determination at 350°C, 30 atm pressure and operating at an oxygen concentration of 5.5%, the reaction product consisted of CO_2, CH_3OH and water. Of the oxidized carbon product 80% consisted of CO_2 but the overall conversion of natural gas was low at 1.33%. Subsequent analysis saw an improvement in the CH_3OH yield to 50% and a natural gas conversion of 6%.

With increase in oxygen consumption, the yields of methanol improved though it was never better than 67% (Table 27 #3).

Another factor was the value of the flow rate. When it was lowered the oxidation was more extensive which benefited the methanol yield. The yield of CO_2 also decreased while CO yield increased.

The conversion of hydrocarbon at 350°C even under the most favorable conditions was only around half of that usually obtained (Table 27 #3). The reaction temperature was raised to 407°C to see if the apparent inhibition of the reaction by the silver wall could be overcome. At this temperature the more usual yields were restored (see Table 27).

In the case of the copper walled reactor, (which was not pre-conditioned) (Run 45) at 352°C, the initial methanol yield was 22% but subsequently fell to 11% with the balance of the oxidized carbon product being CO_2. The conversion of the natural gas remained low at less than 1%. The yield of methanol and % Ngas conversion was not influenced over a period of time, as with silver (Table 28). The reaction temperature was raised to 403°C at which point yields similar to those for silver at this temperature were obtained (Table 28).

The 10% Cu/SiO_2 (Run 46) catalyst did not inhibit the reaction at 350°C as did the copper and silver walls and produced CH_3OH in good yield, but it did not effect reaction at all when the temperature was reduced to 300°C (Table 29).

The 10% Co/γAl_2O_3 (Run 47) on the contrary showed reasonable oxidative activity at 300°C and 4.82% oxygen, albeit directed towards producing CO_2 and H_2O. 5% of the Ngas was consumed and over 80% of the initial oxygen. Raising the temperature of the catalyst bed first to 334° and then 359° improved the amount of Ngas consumed to 11%, using all the oxygen, but CO_2 was the sole oxidized carbon product (Table 29).

Hopcalite (Run 48) proved to be a very active catalyst in terms of overall oxidation but as with the cobalt no CH_3OH was detected. At 300°C and 5.93% O_2 the products were CO_2 and H_2O. The conversion of Ngas was low at 5.5% though all the oxygen was consumed. The catalyst temperature was progressively lowered but with little change in reaction products except for the appearance of CO until at 210°C where the reaction ceased. Raising the temperature to 242°C gave a simlar result to that obtained at 300°C (Table 29).

TiO_2 (Run 49) was unusual in that the consumption of reaction oxygen, and Ngas conversion increased as a function of catalyst temperature. At 300°C only 40% of the available oxygen was utilized but the oxidized carbon product consisted of CO and CO_2 in the approximate proportion of 1:2. As the temperature of the catalyst bed was increased to 407°C, oxygen was completely consumed and the proportion of the CO and CO_2 yields reduced to 2:3 (Table 28b).

When the glass liner was replaced by Teflon (Run 50), the yield of methanol and % amount of Ngas converted at 350°C values were similar to those obtained when glass was used (Table 30).

The antimony doped tin oxide catalyst (Run 51) exhibited reasonable activity at 307°C (Table 31), which was significantly lower than the customary value of 350°C. This activity was short lived however, and could not be restored by increasing or reducing the catalyst temperature.

At 350°C the oxidation reaction, over Stainless Steel walls (Run 52), was not complete in terms of the consumption of O_2 (Table 32). Complete consumption of O_2 was attained at 370°C (Run 53) (Table 33). This may be attributable to the increase in reaction volume to 72 ml (from 39 ml with the glass liner). At 379°C the yields were comparable to those obtained using Teflon or glass and as such the surface may be considered reasonably inert. It should be stressed that the stainless steel tube used in this study was clean and had not been previously exposed to reaction. It would be interesting to investigate the effect that oxidation of the steel surface on the reaction may have in terms of the extent or product distribution of the reaction.

CONCLUSION

With the exception of the antimony doped tin oxide (where activity at 307°C was short lived) none of the catalytic surfaces studied in this Part, improved either the yield of methanol or the reaction conditions (temperature) at which it was produced (Table 34).

Several interesting features were noted. The reaction is influenced by the nature of the wall. The highest methanol yields were obtained over inert walls including glass (Pyrex), Teflon and clean stainless steel. More active wall surfaces such as silver and copper had a negative effect on the reaction, particularly copper, in terms of both the extent of reaction and the methanol yield. The effect was reversible however, and overcome by raising the reaction temperature to 400°C.

The bulk catalysts were in the main overactive, with the exception of the aerogel semiconductors of TiO_2 and Sb/SnO_2. While TiO_2 was active, oxidatively, at 300°C, methanol was never detected in the reaction products (Table 34).

In the case of the antimony catalyst, methanol was produced in reasonable yield at 307°C, approximately 50°C less than normal, but was easily deactivated.

The 10% Cu on SiO_2 catalyst is worth mentioning because of the high methanol yield it returned at 357°C (Table 34).

In summary the oxidation of methane/Natural gas would seem to be almost entirely gas phase and at sub 10% oxygen concentrations the methanol specific yield is good at 85-95% of the hydrocarbon consumed.

Improvement of this situation could occur by operating at a lower temperature or increasing the amount of hydrocarbon converted to methanol at higher oxygen concentrations.

For heterogeneous catalysis to be effective reaction of O_2 with the hydrocarbon must take place at the surface and the semiconductor oxides or the Cu on SiO_2 system appear to be the most suitable for this purpose, based on this limited study.

Because of the gas phase nature of the reaction, homogeneous catalysis would seem to be very worthwhile trying. The simplest method would be to introduce 'initiators' into the reactant gas stream, in low concentrations which would behave in much the same way as the higher hydrocarbons in the natural gas.

PART V. THE OXIDATION OF NATURAL GAS AT LOW PRESSURES AND THE RECYCLE SYSTEM

INTRODUCTION

This part includes the results obtained from experimentation in two major areas: 1. The oxidation of Natural gas at low pressures. 2. The application of continuous recycle system to the oxidation of Natural gas.

The KromoTog chromatograph thermal conductivity detector was recalibrated during this time and the results have been appended (Appendix III).

EXPERIMENTAL

Oxidation of Natural Gas at Low Pressure

Investigations were carried out at 10 atm and atmospheric pressure to determine the effect of reduced pressure on the reaction in terms of methanol specificity and the degree of Ngas conversion.

At the 10 atm level the reaction was studied as a function of flow rate. At the atmospheric level, the variation of oxidized yields with temperature was carried out, and an attempt to determine the optimum reaction temperature made.

Continuous Recycle

Apparatus

A system was designed, incorporating the presently used glass lined reactor, that would permit the removal of oxidized products from the reaction product stream and allow the unreacted components of natural gas to be repressurized to reactor pressure, and reintroduced into the reactor for subsequent reaction.

The recirculation system is illustrated in Figure 9.

The recycle line consisted of four major components.

a) Condenser cylinder. A stainless steel cylinder (500 ml), rated to DOT 1800 psig, and placed in a Dewar to operate at reduced temperature, was connected to the exit of the reactor. The flow to the condenser was controlled by a vernier needle valve (Ideal-Aerosmith V54-1-11) and admission of the reaction products by a regulating/shut off valve (Whitey ORS2).

b) CO scrubber. A 150 ml stainless steel (Recycle III) cylinder (DOT 1800) was packed with activated CuO. The cylinder was placed in a furnace to operate between 300 and 350°C. In Recycle I and II a 17 ml tube was used which was found to have too small a volume.

The CuO would convert the CO to CO_2, by reduction to Cu. It was necessary to activate the CuO (Recycle II and III) for it to be efficient by reducing it in a stream of H_2 at 350-400°C for several hours before oxidizing it in air at 300°C overnight.

Some anhydrous calcium chloride was packed into the entrance of the scrubber to removal residual water from the condenser, followed by a layer of Cu to remove any residual oxygen not consumed by the reaction.

c) CO_2 scrubber. A 150 ml stainless steel cylinder (DOT 1800) packed with Ascarite (NaOH on asbestos) was used to remove the CO_2 produced in the reactor and in the CO scrubber. Some Drierite (anhydrous Na_2SO_4) was mixed with the Ascarite and placed at the exit of the cylinder to remove the water produced by the reaction of CO_2.

The CO_2 scrubber operated at room temperature.

d) Pump/Storage cylinder. A Haskel air driven gas booster (AG15; single acting, single stage) was installed, following the CO_2 scrubber, to repressurize the stripped recycle gas to reaction pressure.

The recycle gas was stored in a modified lecture bottle (volume = 500 ml), which served as a storage cyclinder.

The pump had a swept volume of 100 ml and delivered this amount of gas to the storage cylinder for each stroke of the air driven piston.

Control/Instrumentation

The pressure of the recycle system was monitored at various points using pressure gauges and controlled using vernier needle valves.

The post condenser line pressure, post scrubbers/pre-pump pressure and post pump pressure were monitored by 0-1000 psig LHA gauges (2½" (6.4 cm) diameter).

The recycle gas storage cylinder was fitted with a regulator (ARCO; 0-1500 psig delivery pressure) which was set to deliver a pressure of 450 psig. The flow/pressure of the cycle gas delivered to the reactor was controlled by a vernier needle valve (Ideal-Aerosmith V52-1-11) and monitored by a Heiss Bourdon gauge (6" (15.2 cm) diameter 2 x 360° scale).

The reactor pressure and oxygen flow were monitored as previously described by pressure transducers (Validyne) connected to a Validyne digital transducer indicator (CD223).

Safety Features

The primary concern in this experiment was that it should proceed safely, which basically meant that there should be no oxygen admitted to the pump or any sudden pressure build up.

To ensure that oxygen was not in the post reactor gas it was necessary to maintain the reactor temperature (reaction velocity) at a point where the reactant oxygen would be completely consumed.

Pressure build up, due to ignition or otherwise would be checked by safety relief valves (SRVs - Nupro adjustable), each set to open at a preset maximum pressure. Three SRVs were installed in the system and located as follows, SRV1: At the entrance to the reactor, SRV2: After the condenser and prior to the CO scrubber and SRV3: At the entrance to the Recycle gas storage cylinder following the pump, i.e. at the largest gas volume sources. The SRVs were connected to 1.25 cm i.d. copper pipes which were vented through an outside wall (Figure 9).

It was also important that the flow of recycle gas and the Ngas and oxygen reactant feed be unidirectional. One way check valves were installed to ensure this at the following locations: CV1. Reactor exit line, CV2: At the entrance to the recycle gas storage cylinder prior to the SRV3, CV3: Following the recycle gas control vernier valve, and CV4: Following the Ngas feed control vernier valve. These check valves were in addition to those already installed in the reactor system.

Materials of Construction

Stainless steel was the material chosen to construct the recycle system up to the point of the recycle gas storage cylinder exit, where brass fittings and copper pipe were employed.

1/8" (0.32 cm) stainless steel tubing was used throughout and all fittings were 1/8" (0.32 cm) or reduced to 1/8"(0.32 cm), which was consistent with reactor input lines.

The use of small guage tubing and minimum cylinder sizes meant that the overall volume of the recycle and reaction system would be small. This was advantageous in two respects: 1. Safety and 2. Short recycle time.

Sampling of Recycle and Reactor Gas

The system was equipped with three sampling points: 1. At the exit of the reactor, 2. After the condenser, and 3. After the CO and CO_2 scrubbers.

All three sample points were connected to a common manifold via regulating/shut off valves located at the manifold. The manifold was connected directly, to the previously used capillary line, to reduce the pressure, and linked to the gas chromatograph through a sampling valve. The flow of sample gas was controlled by a vernier needle valve (Ideal-Aerosmith) installed between the manifold exit and the capillary line. These sampling points permitted the analysis of the reaction product gas directly from the reactor (valve S1), after passing through the condenser (valve S2) and after passing through the CO and CO_2 scrubbers before entering the recycle gas storage cylinder (valve S3).

Analysis

The sampled gas was analysed by G.C. using two separate columns. Porapak Q (10'(305 cm) x 1/8"(0.32 cm) ss), at -70°C, was used to analyse for N_2, O_2 and CO while Porapak T was used to analyse for hydrocarbons, and oxidized products, operating in both programmed and isothermal modes.

Operational Procedure

The reaction and recycle systems were pressure checked and safety tested using compressed nitrogen at 50 atm.

The SRVs were set to their respective relief pressures as follows: Reactor SRV1 set to relieve at 40 atm, 10 atm above operating reactor pressure; Post condenser SRV2 also at 40 atm; Recycle gas storage cylinder SRV3 was set to relieve at 50 atm, this was 10 atm higher than the other two SRVs to permit storage of the Recycle gas to above reaction pressure.

By using N_2 alone it was possible to evaluate and approximately set the vernier valves such that the nitrogen could be recycled into the reactor, detected by the increase in the reactor pressure transducer.

It was assumed that mixing of the supply Ngas and Recycle gas feeds, and consequently reactor pressure, could be controlled by vernier needle valves in each line prior to entering the mixing Tee through opposing check valves.

Operation of the recycling system under reaction conditions initially involved the setting of the reaction mixture, Ngas + O_2, to the desired concentration and flow rate. Initiation of the reaction was effected by increasing the reactor temperature to 350°C in the normal way. The reaction was monitored by G.C. until it had reached steady state and the conversion was noted (Tables 42, 44 and 47).

The reaction products were then admitted to the condenser by opening valve A (see Figure 9).

Once the pressure of the gas in the condenser had built up to around 10-14 atm the gas was admitted to the CO and CO_2 scrubbers by opening valve B.

The gas entered the Recycle gas storage cylinder by passing through the one way check valves in the head of the gas booster. The pressure was allowed to build up in this way, to around 20 atm, to the point where back pressure, in the recycle line, caused the reactor pressure to increase.

From the initial opening of valve A, this would take in the order of three hours to occur.

At this point the gas booster was stroked once. Typically one stroke of the pump boosted the recycle gas pressure by about 3.4 atm and reduced the pre-pump pressure by an amount less than this (see data in Appendix II).

This procedure would be repeated 3-4 times an hour. Once the delivery gauge of the Recycle gas storage cylinder (RGSC) reached 30.6 atm, the shut off valve on the regulator was opened to admit the gas to the reactor. The flow was controlled by a vernier valve and the recycle gas line pressure monitored by the Heiss gauge. Typically this would increase to between 28-28.6 atm before entering the Ngas feed line. The recycle gas would first mix with incoming Ngas from the supply cylinder before being mixed with oxygen in the mixing cross preceeding the reactor.

The addition of recycle gas to the supply Ngas feed caused the reactor pressure to increase. In order that the reactor be maintained at fairly constant pressure the vernier valve controlling the flow of Ngas through the Recycle-Ngas mixing Tee was closed down to the point where the reactor pressure was re-established at its original value.

The amount of Recycle gas could be increased by opening the recycle gas vernier valve. The Recycle-Ngas mixture could be set in this arbitrary way and the incremental increases in reactor pressure for each Recycle gas addition added and used to give an estimate of the proportion of Recycle-Ngas. Once the desired ratio was achieved the Recycle and Ngas control verniers were left at their set positions.

The system could now be said to be operating in a continuous recycle mode.

Analysis of the reaction gas, for O_2, and the recycle gas for CO was made approximately every hour, once the system had reached operating equilibrium. Monitoring of the reaction temperature was very important as this determined the consumption of oxygen.

Since all three sampling points were connected to a single manifold it was essential that the manifold be well purged between analyses of samples from different points, particularly when monitoring for CO. This resulted in a loss of reactant as well as product for some cases and only unreacted product in others.

RESULTS AND DISCUSSION

Low Pressure Oxidation

It was considered that a reduction in the reactor pressure would not dramatically reduce the yields of oxidized products. It was thought that the extent of oxidation would be reduced, due to a lowering of the reaction velocity, but that this might favour the production of methanol over that of CO and CO_2.

All of the low pressure investigations were carried out in the glass lined reactor.

At 356°C and 10 atm, the yield of methanol was high (Table 35) and the distribution of the oxidized yields was comparable to that obtained at 30 atm (Table 2, Appendix 1). Comparison of the 10 and 30 atm results with those obtained at 50 atm show that the methanol yield had increased at the expense of CO_2, the production of which appears to be pressure dependent (Table 1, Appendix 1).

At 356°C not all of the available O_2 was consumed, but O_2 was not detected in the products at 411°C (Table 36). Percent conversion of Ngas was not as high as expected, assuming complete reaction of the Ngas with 4.22% oxygen.

Analysis of the reactants after the experiment showed that the oxygen concentration had decreased during the course of the investigation from 4.22% to around 1%. Evidently, working at these lower pressures entailed adjustment of the coarse O_2 needle valve controller to a new setting to permit a constant O_2 supply.

Nevertheless, the results were encouraging and at 411°C CO_2 did not appear in the reaction products.

Rather than increase the reaction velocity, by operating at higher temperatures, a study was designed to observe the effect of varying the flow rate at 350°C, on the extent of reaction. At 10 atm the space velocity would be substantially more (lower residence time) than at 30 atm for the same volume flow rate at NTP.

Interestingly, at high flow rates (short residence time), whilst, the extent of reaction was low, methanol was the sole oxidized carbon product (Table 37). The consumed 0_2 concentration was low, as expected, dropping from 7% to 6%.

As the space time was increased (increased residence time) the extent of the reaction increased (Table 38) and at 4.5% 0_2 (Table 39) oxygen was completely consumed, albeit at 374°C (Figure 10). Yields of $C0_2$ remained low and the methanol yield was around 90%. This kept the methanol specific yield high at 6.55% of the 7.23% Ngas converted.

At atmospheric pressure it was necessary to raise the temperature substantially from 350°C to initiate reaction. At 439°C (Tables 40a)-d)) just less than half of the available 0_2 was consumed, though the amount of Ngas converted was correspondingly lower than expected on this basis, and these amounts did not increase greatly at 457°C (Table 40e)). The product distribution was quite different to that obtained at 10 atm, with the CO yield increasing with temperature at the expense of methanol.

At 490° and 502°C this trend continued, as would be expected for complete consumption of 10% reactant oxygen (Figure 11). At 502°C the CO and CH_3OH yields were equal, at under 50% (Table 40g)). At 490°C methanol was preferred (Table 40f)) to CO. 8% 0_2 was consumed in both determinations at 477° and 457°C (Table 41) and while the methanol yield at 457°C was good, at 82%, it was inconsistent with that obtained previously (Table 40e)). In summary, methanol can be produced almost exclusively by reducing the reaction pressure to around 10 atmospheres and operating at a relatively high flow rate. Conversion of the hydrocarbons will be low however, but the need to remove oxidized carbon products other than methanol would be unnecessary. At longer residence times, up to 5% O_2 can be incorporated into the product yield to give values comparable to those found at 30 atm and above.

Reduction of the reaction pressure to the atmospheric level would not appear to offer any immediate advantages because of the associated increase in reaction temperature, required to initiate the reaction. The optimum atmospheric temperature appears to be between 450-480°C.

Continuous Recycle

The first recycle experiment was primarily designed as an exploratory investigation to determine more precisely the settings of the various controls over those obtained using N_2, and to gain an appreciation of the pressure drops and consequent frequency of operation of the gas booster in a reaction situation.

In addition the efficiency of the condenser, the CO and CO_2 scrubbers could be assessed.

The initial oxygen concentration was set at less than 3%, to ensure its complete consumption, in case reaction conditions should alter during the run.

The reaction analysis, at 32.5 atm, showed that methanol was produced in good yield, all the O_2 was being consumed and the expected amount of Ngas was being converted (Table 42).

The condenser, in this experiment (Recycle I) was placed in a Dewar of ice to prevent the possibility of the condensation of ethane and propane at 30 atm by operating at too low a temperature.

The CuO in this experiment was packed into a stainless steel tube (1.27 cm o.d.) of 17 ml internal volume.

Sampling of the system during the run for O_2 showed that it was being completely consumed (Table 43a)1). The actual operation of the recirculator over long periods of time depended upon this.

Detection of CO in reaction amounts confirmed that it was not being removed efficiently though CO_2 was (Table 43a.3). This G.C. analysis is shown in Figure 12.

The CO scrubber was estimated to be operating at around 15% efficiency. It was thought that the CuO would need to be activated, in subsequent experiments.

Analysis of the post-condenser gas revealed that methanol and water were not being effectively removed (Table 43a)2) and suggested that the condenser temperature be substantially lowered.

Because of these inefficiencies the Recycle phase of the experiment was run for 1 hour and 10 minutes before being stopped.

The volume of liquid product collected was approximately 1 ml, and upon analysis, by G.C. and NMR, found to consist of methanol, water and possibly formaldehyde (Table 43b).

The second Recirculation run incorporated two major modifications: 1. The maintenance of a temperature of -50°C, about the condenser ('controlled' dry ice/ethanol), and 2. Packing the CO scrubber with activated CuO.

The initial reaction analysis (Table 44) showed O_2 was completely consumed although the specific methanol yield was less than expected based on 5% O_2.

The recirculator was run for 6 hours. O_2 in the reaction stream was not detected during this time (Table 45) (Figure 13(i)). It was estimated that 60% of the reaction CO was removed and all of the CO_2. This was an improvement over that in the previous Recycle experiment (Figure 13(ii)).

Unfortunately problems with the G.C. at this time meant that it was not possible to analyze the post condenser or recycle gases for H_2O and CH_3OH during the course of the experiment.

Analysis of the collected condenser gas after the experimental run showed that there was essentially no difference in composition (Table 46.1a) when compared with the initial reaction product composition (Table 44).

Approximately 3 ml of liquid product was collected and analysis by G.C. confirmed the presence of HCHO in 3-4% amounts (Table 46.1b)(Figure 14) and corroborated by ^{1}HMR and ^{13}C NMR (Table 46.1b).

The stored Recycle gas contained large amounts of H_2O and CH_3OH (Table 46.2), though the CO level had been reduced by 61% over that produced in the reaction.

Again the condenser proved inadequate. An increase in the amount of CuO, however, would probably effectively eliminate CO.

The cold surface area of the condenser was increased by packing the central section of the cylinder (approximately one third of its volume) with Ni/Ag wool (Kurly Kate). The temperature of the condenser would be kept at -50°C.

The third recirculation run was carried out at an O_2 concentration of 4.2% and an initial yield of methanol of 86% (Table 47)(Figure 15(i)).

Analysis of the Recycle gas after the first six hours of operation demonstrated that O_2 was completely consumed and CO effectively removed (Table 48, Figure 15(ii)).

Reaction analysis after 24 hours operation revealed that the methanol yield had decreased (Table 49) from its initial value (Table 47) and that more CO was being produced, but the reaction was essentially proceeding fairly well (Figure 15(iii)).

Some typical operational data is included in Appendix II to demonstrate that the recycle system ran fairly smoothly without too many fluctuations, for a relatively simply designed system.

The chromatograms, although not quantitative, demonstrated that methanol and water were being removed, albeit not completely, from the reaction product stream (Figure 15(iv)).

Just prior to the shutdown of the Recirculator a determination of the N_2 build up (in Ngas), was made and the post condenser gas analysed (Table 50). N_2 had increased, though not greatly, from an initial N_2/CH_4 value of 0.58 (Table 47) to 0.61 after 24 hours (Table 49), to 0.7 at the end of the run, after 46 hours, equivalent to 20% of the initial value.

The post condenser gas contained approximately 1% methanol, but a little over 10% water (Table 51). Comparison of this value, for methanol, with that in the initial reaction mixture (Table 47) represents a 6 fold reduction, but only a 3 fold reduction compared with the amount of methanol produced after 24 hours (Table 49).

The Recirculator was shut down after 46 hours continuous operation.

The condenser contents, both gaseous and liquid, were analysed together with the contents of the stored Recycle gas (Table 52).

The Recycle gas contained no CO or CO_2 and both scrubbers had worked efficiently. Methanol and water were both detected, and the methanol concentration was higher than that found in the post condenser gas.

The condenser gas contained less than 1% methanol but 10% water.

The total volume of the liquid fraction collected was approximately 30 ml. This figure represented the amount drained from the condenser and that extracted with ethanol. Extraction of some of the product was necessary because a significant amount of product was retained by the Ni/Ag wool in the condenser. Even after two extractions with ethanol, in which the liquid oxidized products were quantified by G.C., the odor of the product was detected on the wool, which was still wet when removed. It was found by extraction with ethanol that as little as one third of the 10 ml extract was recovered. Allowance was made for this, but the 30 ml figure arrived at was a conservative one and the actual value may be somewhat higher.

The liquid fraction contained approximately 3% HCHO and equal amounts of CH_3OH and H_2O. The identity of HCHO was again confirmed using a calibration sample, by G.C. The concentration of HCHO was also determined spectrophotometrically and a value of 5% obtained (Table 52).

Three independant estimates of the consumed Ngas, including Recycle gas, were made. The first was made by determining the flow rate at NTP of the reactor exit gas following shutdown of the Recirculator. The vernier control valve at the reactor exit was adjusted, to give the same transducer pressure reading used during recirculation, allowing the Ngas (in the absence of O_2) to flow to atmosphere. This value was simply multiplied by the number of hours of operation to arrive at the volume of gas used.

The second method involved counting the number of times the gas booster had been stroked. Knowing the swept volume (100 ml) and the input pressure, a value of the volume of gas was again calculated.

Finally an approximate evaluation was made from an estimate of the pressure drop of the Ngas supply cylinder and a knowledge of the internal volume of the cylinder.

All three values were in reasonable agreement so that an average of the three was taken (see Appendix II). Based on this value however, (314 liters NTP) the yield of methanol was much less than expected, (5.5%), allowing for the residual gas in the system, at shutdown. An estimate of the molar volume of CH_3OH not trapped in the condenser was made, and also subtracted from the volume of gas used. The yield of methanol calculated on this basis was 6.9%, still low.

Possible explanations, for the reduced yield of methanol, include a small but constant leak of reactant gas and product. Loss of methanol and hydrocarbon would decrease the volume of methanol collected and increase the value of Ngas consumed. The leak would have to be small otherwise the system could not have attained operating pressure in the recycle system.

The time taken to fill the condenser, based on the estimated flow rate of 100 ml/min, and allowing for the removal of water and methanol, suggested that a leak could not be greater than 0.5 l/hour. This would improve the methanol yield to 7.8%.

Even after making these allowances the yield of methanol would be low. The condenser was certainly not 100% efficient and it was quite likely that the untrapped methanol was oxidized to CO and CO_2 over the CuO catalyst, or further when it reentered the reactor. It is possible, and could be verified, that some of the natural gas, certainly the higher hydrocarbons, may have been consumed/oxidized by the CuO.

Consumption of ethane, and propane, which was barely detected in the recycle gas, would affect both the production of methanol and increase the volume of gas used.

In conclusion the Recirculator has been demonstrated to be fully operational, relatively simple to control, reliable and could be readily automated.

Some fine tuning of the system is required however, to obtain the 60-70% yield of methanol that should be possible.

CONCLUSION

Reduction of the reactor pressure, and hence reaction velocity, favored the yield of methanol by keeping CO and CO_2 yields very low. However, the amount of Ngas converted was lower at 10 atm than at 30 atm. Raising the temperature to 374°C and operating at lower flow rates ensured complete consumption of the available oxygen and yields which compared well with those obtained at 30 atm.

Operating at reduced pressures, while favoring methanol, would impose an upper limit on the extent of the hydrocarbon oxidation, because of the lesser amount of oxygen that will react. Nevertheless the results demonstrate that low pressure supplies of Natural gas could be converted to methanol in good efficiency.

The high yield of formaldehyde was surprising and can be explained if one assumes that some methanol was passing through the recirculator and was oxidized to H_2CO.

More experimentation is required with the Recirculator to improve the collection efficiency of the condensable fraction and it should be run for longer periods of time before a more critical assessment of the overall efficiency of the process is made. The operational reliability of the apparatus was very good however, and permitted recirculation under good control and safety, and could be readily adapted for future experimentation.

PART VI ECONOMIC STUDY OF REACTION PROCESS

INTRODUCTION

The purpose in preparation of this section is to qualitatively analyze the economics and thermodynamic efficiency of a methanol producing plant based on the direct controlled oxidation of natural gas.

A digital program using the Fortran computing language is developed to simulate the methanol production process as depicted in Figure 16. Chemical reactor data compiled from operation of a bench scale reactor is used to describe reactor behavior, based on the chemical reaction:

$$a\ CH_4 + b\ O_2 \longrightarrow c\ CH_3OH + d\ CO + e\ CO_2 + f\ H_2O$$

No attempt is made to optimize processing parameters in the thermal and economic analysis. For each set of experimentally determined reactor operating data, process simulation is done to yield conservative values for overall energy efficiency and cost per litre methanol produced.

THE SIMULATION PROGRAM

A digital computing program is constructed using the Fortran computing language to simulate the operation of a commercial scale methanol plant based upon the chemical reaction previously introduced.

The main calling program is named 'Master' and controls the execution of calculations. Execution of this program begins with initializing variables and reading of input data, followed by sequential execution of process unit simulating subroutines.

Process unit simulating subroutines are repeatedly called upon until recycle and purge streams converge to a steady state value. Once steady state is achieved values of temperature, pressure and component flowrates of each stream are printed, followed by calculation and output of thermodynamic and economic values.

The flow of logic is shown below and in Figure 17. Detailed description of calculation method used in each subroutine is available from the authors.

The reaction assumed was

$$a\ CH_4 + b\ O_2 \longrightarrow c\ CH_3OH + d\ CO + e\ CO_2 + f\ H_2O$$

where for a hydrogen balance $4a = 4c + 2h$

a Carbon balance $a = c + d + e$

an Oxygen balance $2b = c + d + 2e + h$

The selectively = c/a and the value of h is calculated from $h = 2(a-c)$ since the value of the water analysis was uncertain.

A daily feed rate of 1 million cubic feet (10^6 cu ft) (2.8×10^7 l) of natural gas was assumed. Standard heat capacity data were used. The water/alcohol mixture was redistilled to produce 99.9% methanol. Heat exchangers were used where appropriate and costs were determined from Reference 10. The capital costs were amortized over 15 years at a 12% annual interest rate.

The cost of electricity energy was set at $.06 CAN per KWhr (11). The feed cost was set at $4.00 CAN/1000 SCF ($2.8 \times 10^4$ l) (12). Oxygen was set at \$1.11 CAN/1000 SCF (2.8 x 10^4 1). Other costs include absorber and distillation column (10), compressors and piping (10). Excess heat was credited to the process by its composition equivalent of natural gas.

RESULTS OF SIMULATION

Results of digital simulation on 5 sets of reactor operating data are given in Tables 53a,b,c,d & e for a few examples. Thermodynamic efficiencies, depending upon reaction conditions, range from 67% to as high as 85.5%, requiring no external heating source. Production costs calculated, depending upon reaction conditions, range from \$0.1843/litre to \$0.1178/litre CAN or \$0.45 to \$0.70 CAN/US gal. Present costs of methanol are at about \$0.40 to \$0.50 US per US gal. Thus this process compares favorably with present larger plants.

DISCUSSION OF RESULTS

This qualitative thermodynamic and economic analysis of methanol production by the direct controlled oxidation of natural gas is based upon several assumptions as discussed below:

1. Natural gas feed of 99.5 mol % methane, 0.5 mole % nitrogen, at a cost of \$4.00 CAN/1000 scf (2.8 x 10^4 1) (except for natural gas runs).
2. Pure oxygen feed at a cost of \$1.11 CAN/1000 scf (2.8 x 10^4 1).
3. Electrical cost of \$0.06 CAN/KWHr.

4. Natural gas and oxygen feed is supplied at 25°C and at reactor pressure.
5. Process gases behave as ideal gases: This assumption will increase calculated compression work requirements and volume occupied per kilogram relative to a real gas system.
6. Maximum reactants' nitrogen mole fraction of 0.16.
7. Heat generated by reaction is saleable at a price equal to the cost of methane required to produce an equivalent amount of heat.
8. Reactor geometry is that of a tube bundle of 2 inch diameter tubes in a shell and tubeheat exchanger, with heat transfer possible so that coolant leaves reactor unit at or near the reactor temperature.
9. 10°C approach at reactant preheater: In the Xheat heat exchanger unit, reactants are heated to 10°C below that of the product stream (stream 2).
10. Latent heat of condensation of any condensible species that may condense in the Xheat heat exchanger is neglected: This simplifying assumption will tend to decrease calculated thermodynamic efficiency, and may also lead to small under-estimation of cooling costs for stream 3 at the condensing drum.
11. Condensing drum process behaves according to Raoult's Law, condenstaiton of methanol-water solubility of gas components is negligible.
12. Recycle gas compression is adiabatic and 70% efficient. Compressor motor is 80% efficient.
13. Cost of cooling water is neglected.

14. Distillation reflux ratio specified as 1.3 times the minimum reflux ratio.
15. McCabe-Thiele method of distillation analysis used with the assumption of constant molal overflow.
16. 10°C approach between distillation reboiler recirculating liquid and 30 psig saturated steam as heating medium.
17. Equipment cost approximations are valid.
18. Pumping costs for distillation and absorption processes are neglected.
19. Absorption column make-up water costs neglected.

Given application of these assumptions it is evident that economic optimization of the process is not attempted in this report. Variables such as plant feed rate, reactor geometry and size, maximum specified reactant nitrogen concentration, reactant preheater size, distillation reflux ratio, reboiler steam pressure and recirculating liquid rate, cooling water costs or processing method have not been varied to aid in exploration of optimum design.

Although economic optimization is beyond the scope of this evaluation results show that cost of production is most strongly dependant upon feed percent conversion to methanol, distillation heat and compression work requirements for the design of Figure 16. Thus, since % conversion of methane to methanol per reactor pass, distillation heat and compressor work requirement are a direct function of reaction conditions, simulation results show a first approximation to optimum reaction conditions and resultant thermal efficiency and costs.

Results are output separately as cost per litre methanol produced for each equipment unit and for costs of natural gas, oxygen, electricity, and energy credit. Hence, if the reader wishes to consider use of different costs of other operating parameter, a change can readily be seen on the overall costs or thermal efficiency of production.

CONCLUSIONS

Production of methanol by the direct controlled oxidation of natural gas appears to be an economically attractive method which displays several advantages over the commonly used synthesis gas production method.

One such advantage is that ony one chemical reactor is required whereas the synthesis gas route is a two step process requiring sequential reactors. Thus, the direct controlled oxidation route requires less equipment.

A second important advantage is that no external heat source is required as the process produces surplus energy. In addition, if excess process heat is utilized, calculations done in this report show that thermodynamic efficiencies of the process reach as high as 85.5%. This compares favourably to production by the synthesis gas route which has thermodynamic efficiencies of 61% (13).

In conclusion we see that the direct controlled oxidation of natural gas to product methanol is a process which appears to be economically advantageous over present commonly used methanol manufacturing methods.

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APPENDIX I.

A. Oxidation of Ngas: Glass lined reactor (Revised results).

Table 1

Run 42

Pressure = 50 atm Temp. = 350°C

Flow Rate = 12 $(\text{reac. vol.})^{-1}$ O_2 conc. = 5.7%

S.T. (reactor) = 261s $(\text{reac. vol})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.375	-	0.95	64.80	0.78	0.85	0.285	21.62	10.62
%Cout			1.25	82.20	1.02	1.06	0.35		14.19
%Coxid			7.95 ± 0.56		0.76 ± 0.05				89.65 ± 0.90
C/N_2			2.55	167.75	2.06	2.19	0.72		29.00
±			0.03	10.64	0.04	0.15	0.07		2.50
O_2/N_2		-	1.27		2.06			10.81	14.50
±			0.01		0.04			0.94	1.25

%Ngas conversion = 14.26 ± 1.04

%C bal = 90.18

%CH_3OH converted = 12.79 ± 1.06

Oxidation of Ngas: Glass lined reactor.

Table 2

Run 43

Pressure = 30 atm   Temp. = 350°C

Flow Rate = 12.1s(reac. vol.)$^{-1}$ O_2 conc. = 4.84%

S.T. (reactor) = 168s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.33	-	0.92	59.30	0.73	0.84	0.33	25.53	12.01
%Cout			1.24	80.00	0.98	1.13	0.45		16.20
%Coxid			6.93 ± 0.45		1.00 ± 0.37				92.07 ± 0.66
C/N_2			2.88	183.50	2.18	2.41	0.78		38.74
±			0.12	3.93	0.06	0.12	0.16		2.94
O_2/N_2			1.44		2.18			38.56	19.37
±			0.06		0.06			-	1.47

%Ngas conversion = 13.36 ± 1.77

%C bal = 106.02

%CH_3OH converted = 12.53 ± 1.51

B. Calibration of Burrell Kromo-Tog Thermal Conductivity Detector.

The TCD was calibrated with respect to CH_3OH, CO and N_2. CH_3OH was injected in microlitre quantities using a Hamilton syringe equipped with a Chaney adaptor for repetitive injection. However, there will have been some error associated with this method. CH_3OH was injected onto the column (Porapak S 100/120 10' x 1/8" o.d. SS) at 180°C, the temperature at which it would normally elute. The gases were injected using a gas syringe in millilitre quantities at room temperature as they would be in a reaction analysis. These compounds were injected at a variety of amplifier attenuation settings.

Table (i) CH_3OH

Volume Injected (μl)	T.C. Atten.	Peak Area
0.4	x32	1171.60±20.95
0.3	"	835.0±6.12
0.2	"	496.87±18.69
0.1	"	24.50±0.0
0.4	x64	561.25±41.45
0.3	"	420.0±5.0
0.2	x16	1079.28±14.98
0.1	"	503.75±17.10
0.1	x8	94.0±10.80

Table (ii) CH_4

Volume Injected (ml)	T.C. Atten.	Peak Area
0.4	x64	533.75±9.60
0.3	"	332.5±7.50
0.2	"	223.33±2.30
1.0	x128	531.66±2.36
0.5	"	255.0±12.25
0.2	"	115.0±0.0
1.0	x256	278±6.23
0.5	"	255±12.25
0.2	"	60.0±0.0
0.2	x32	440.0±8.16
0.1	"	93.33±2.36
0.1	x16	395.0±4.08

Table (iii) N_2 and CO

a) N_2	Volume Injected (ml)	T.C. Atten.	Peak Area
	0.4	x128	28.5±0.25
	0.2	"	14.0±0.0
	0.2	x64	375.0±4.08
b) CO	1.0	x256	39.0±0.0
	0.2	x64	270±0.0
	0.1	x32	24.0±5.0

These results were plotted out in terms of average peak area against volume of compound injected (Figure (i) - (iii)). The slope of the curves was determined and converted into a peak area/mole figure to allow the detector sensitivities to be compared (Table (iv)).

no. of moles of CH_3OH in $1\mu l$ $= \dfrac{\text{inj. vol x density } CH_3OH}{\text{mol. wt.}} = \dfrac{1.0 \times 0.7914 \times 10^{-3}}{32}$

$= 2.47 \times 10^{-5}$ mol

no. of moles of gas in 1 ml = inj. vol/22415

= 1/22415

$= 4.46 \times 10^{-5}$ mol

Table (iv). Relative sensitivy of detector to various compounds.

Compound	Atten.	Flow Rate (ml/min)	Slope From calib. curve (area units/unit vol)	Sensitivity (area units/mol)
CH_3OH	x16	18.2	5393	2.183×10^8
	x32	"	2696	1.092×10^8
	x64	"	1400	5.668×10^7
CH_4	x32	40.0	2200	1.085×10^8
	x64	"	1080	5.339×10^7
	x128	"	530	2.603×10^7
	x256	"	275	1.356×10^7
N_2	x64	"	1375	6.780×10^7
	x128	"	708.3	1.587×10^7
CO	x32	"	2400	1.183×10^8
	x64	"	1350	6.657×10^7
	x256	"	390	1.923×10^7

Comparison of the sensitivity values for CH_4 and CH_3OH shows that the detector is less sensitive to CH_4 by a factor of 0.9419 at an attenuation of x64 and by 0.9936 at x32 averaging to 0.9677.

Application of this factor to the % CH_3OH converted from CH_4 and CH_3OH as a % of carbon products (Cout) brings them into better agreement (see Table 11b. revised).

We can say therefore that the results for methanol are subject to an error of around 3.5% on account of the slight difference in sensitivity between CH_3OH and the major compound with which it is compared CH_4.

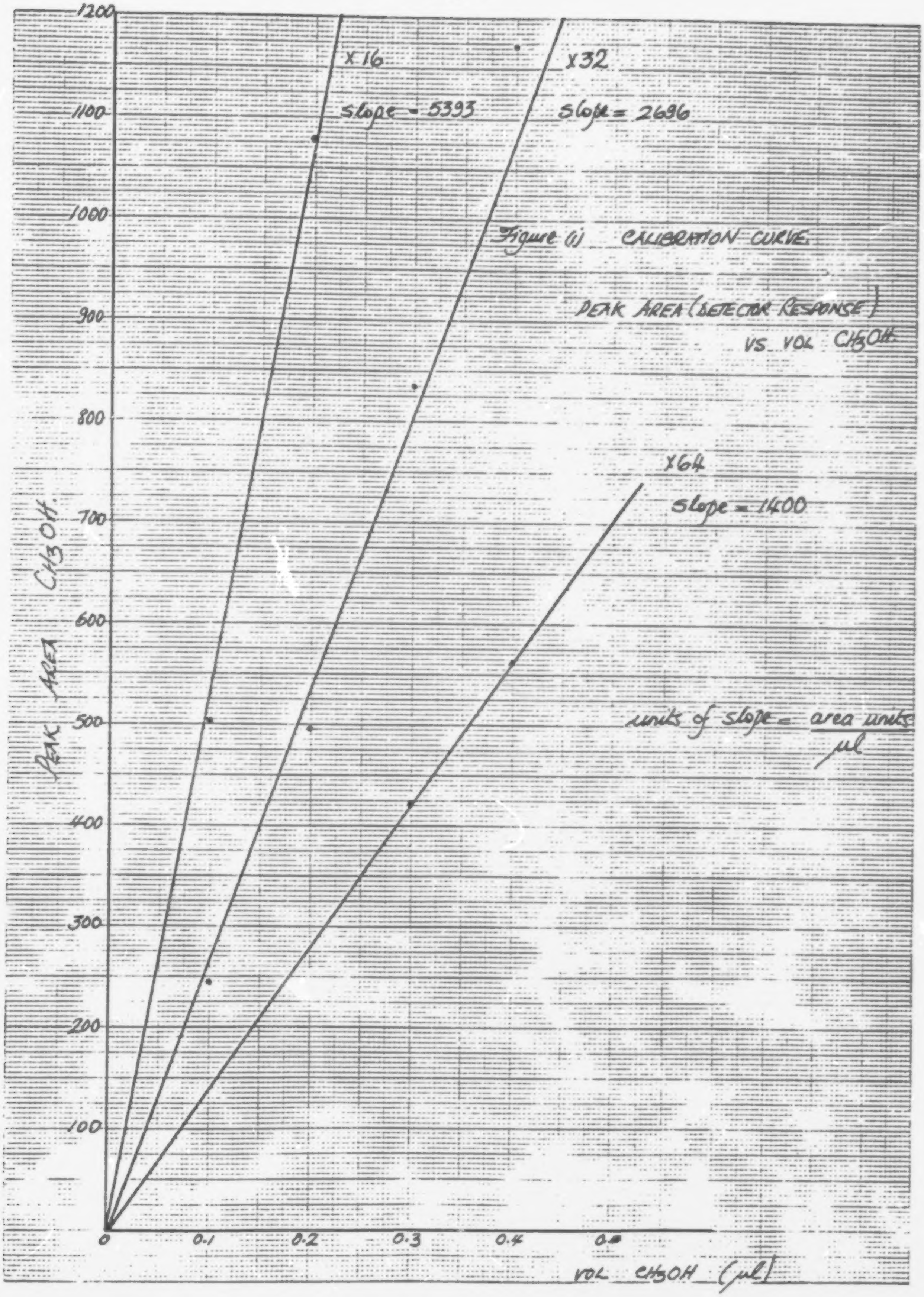


Figure (i) CALIBRATION CURVE.

PEAK AREA (DETECTOR RESPONSE) VS VOL CH3OH.

10 X 10 TO THE CM

Figure (ii) CALIBRATION CURVE. PEAK AREA (DETECTOR RESPONSE) VS VOL. CH4

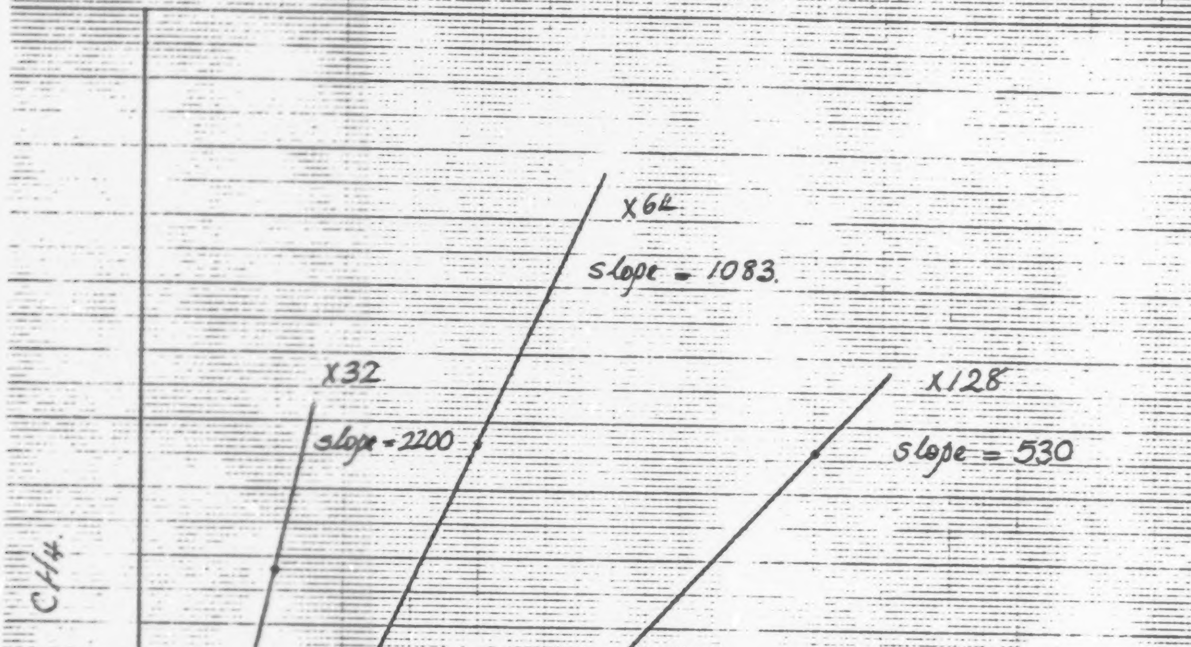
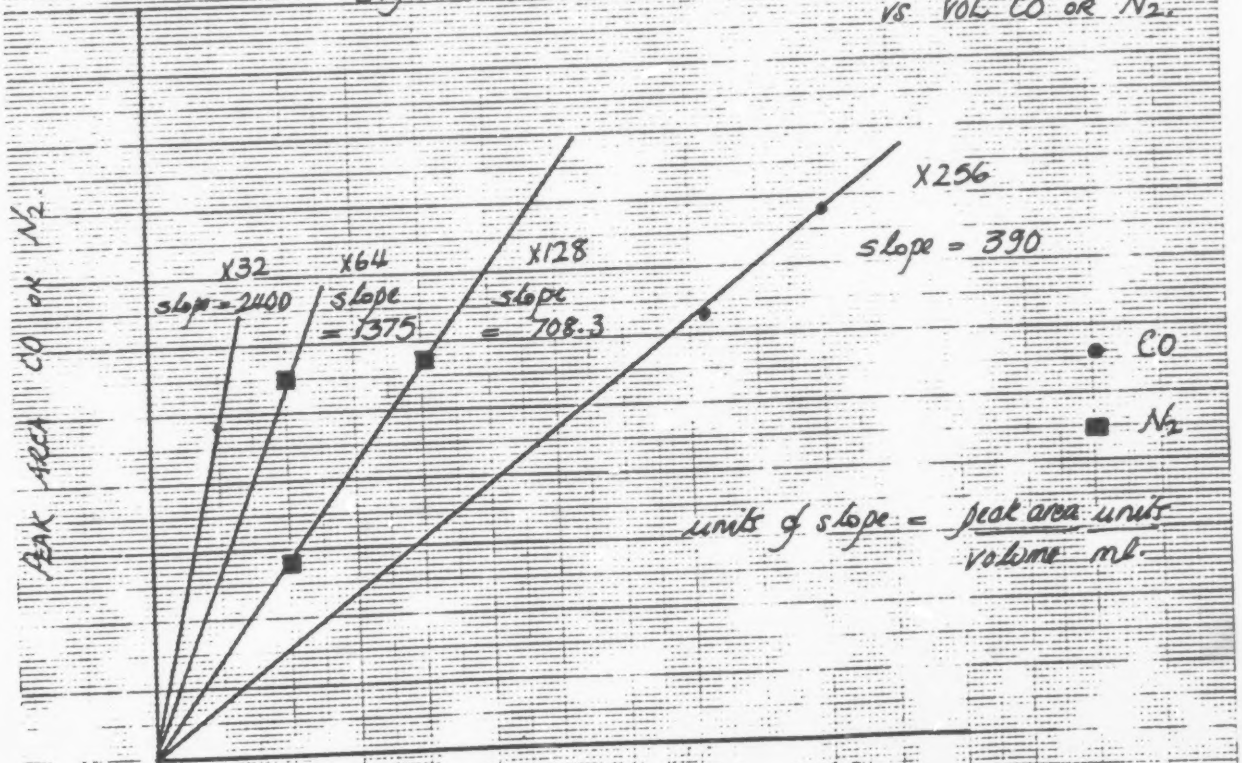


Figure (iii) CALIBRATION CURVE. PEAK AREA (DETECTOR RESPONSE) vs VOL CO or N_2.



10 X 10 TO THE CM

APPENDIX II.

Typical Operating Data Obtained During Recirculation III.

Abbreviations. pP & CP = Pre-Pump & Condenser Pressure RGSP = Recycle Gas Storage Pressure; RGdP = Recycle Gas Delivery Pressure; RP = Reactor Pressure(transducer units; 1 psig = 0.01944 units) S = no. of times pump stoked; G.C. = G.C. analysis.

Time	pP & CP (psig)	RGSP (psig)	RGdP (psig)	RP (trans. units)	S	GC	Comment
20:30	295	545	415	9.48	1		CO(vs),no O_2
	270	600	410	9.37			
20:45	295	540	414.5	9.48	1		
	275	605	411	9.38			
21:00	295	545	415	9.38	1		
	275	605	412	9.42			
21:15	295	550	415	9.48	1		Reactor temp = 386°C
	275	610	410.5	9.38			
21:30	295	550	415	9.49	1		
	275	615	410	9.36			
21:47	305	545	416	9.50	1		no CO, no O_2
	280	595	411	9.38			
22:00	305	545	414.5	9.47	1		Reactor temp = 400°C
	275	605	410	9.37			
22:15	300	550	415.5	9.48	1		
	280	615	410.5	9.38			
22:30	305	550	416	9.50	1		Reactor temp = 386°C
	280	600	411.5	9.39			
22:47	300	550	415	9.49	1		no CO, no O_2
	280	610	411	9.39			
23:00	300	560	416	9.51	1		
	280	610	N.R.	9.40			
23:15	300	560	416	9.51	1		
	280	610	N.R.	9.40			
23:30	300	560	416	9.51	1		
	280	610	N.R.	N.R.			
23:47	300	560	417	9.53	1		no CO, no O_2
	280	610	N.R.	9.40			

Time	pP & CP (psig)	RGSP (psig)	RGdP (psig)	RP (trans. units)	S	G.C.	Comment
00:01	310	560	416	9.51	1		Reactor temp
	280	620	N.R.	9.41			= 378°C
00:16	300	570	417	9.54	1		
	280	620	N.R.	N.R.			
00:33	300	560	416	9.51	1		
	270	620	N.R.	9.39			

Determination of Ngas consumption

Run 63 - Recirculation III

Method 1. Vol. gas consumed = Flow Rate x Time

Flow Rate Ngas + Recycle Gas at Reaction Pressure (9.81 - 9.79 trans units).

= 113.2 ml/min NTP

Recycle duration = 46 hours

Amount of gas used = 46 x 60 x 113.2

= 312.43 litres

Method 2. Vol. gas consumed = pump capacity x no. of strokes

Pump (cylinder) = 100 ml

Input pump pressure = 300 psig (20.41 atm)

No. of pump strokes = 162

Vol. gas consumed NTP = 100 x 162 x 300/14.7

= 330.61 litres

Method 3. Vol. gas consumed = pressure drop of supply cylinder

Ngas cylinder volume = 44 litres

Ngas cylinder pressure = 2250 psig (full)(153.1 atm)

Pressure drop during Recycle = 100 psig

Vol. gas Ngas cylinder NTP $= \frac{2250 \times 44}{14.7}$

$= 6734.7$ litres

Fraction of gas vol used $= \frac{100}{2250} \times 6734.7$

$= 299.32$ litres

Average of Ngas consumed = 314.12 ± 12.83 Litre NTP

Determination of Apparent CH_3OH yield:

Vol CH_3OH = 15 ml (liquid)

$$= \frac{15}{0.7914} \times \frac{22.415}{32}$$

$= 13.28$ litres (gaseous)

$$\% \text{ yield} = \frac{13.28}{314.12} \times 100$$

$= 4.23$

Actual yield CH_3OH =

$$\frac{\text{vol. } CH_3OH}{(\text{vol. gas consd.}) = (\text{vol. } H_2O) - (\text{vol. gas in system})} \times 100$$

$$= \frac{13.28}{314.12 - 33.10 - 39.46} \times 100$$

$$= \frac{13.28}{241.56} \times 100$$

$= 5.5\%$

Allowances:

1. Methanol present in post condenser gas in 1% concentration

   = 3.14 1

   $\% \; CH_3OH \text{ yield} = \frac{16.42}{238.42} \times 100$

   = 6.89%

2. Possible leak in system

   maximum leak estimated at 0.5 1/hour

   46 hours operation at 0.5 1/hour

   = 23 1

   Assuming CH_3OH = 10% yield converted (methanol specific yield)

   then % yield $CH_3OH = \frac{16.42 + 0.23}{238.42 - 23}$

   = 7.73%

APPENDIX III

Recalibration of Burrell thermal conductivity detector.

Compounds calibrated = CH_4, CO, CO_2, C_2H_6, C_3H_8, H_2O, CH_3OH and C_2H_5OH.

Compounds were calibrated by injecting known volumes onto a Poropak T column (normally used for analysis) at their respective retention (elution) temperatures.

(i) ice - room temperature CH_4, CO

(ii) 150°C remaining compounds

The data was plotted graphically in terms of the number of moles of compounds as a function of its area.

(i) CH_4 Atten. = x168

volume (ml)	no. of moles ($x10^5$)	average area (integ. units)
1	4.46	5330 ± 91.2
0.6	2.28	3106.6 ± 18.8
0.4	1.78	2066.6 ± 6.8
0.8	3.57	4320 ± 163.2

CO Atten. = x16

volume (ml)	no. of moles ($x10^5$)	average area
0.6	2.68	5466.7 ± 75
0.4	1.78	3480 ± 32.6
0.3	1.335	2373.3 ± 123.6
0.2	0.89	1770 ± 41.2

(ii) CO_2 Atten. = x16

volume (ml)	no. of moles ($x10^5$)	average area
0.6	2.68	10053 ± 247.3
0.5	2.23	8693 ± 100
0.4	1.78	5906.7 ± 114.7
0.2	0.89	2813 ± 61.8

C_2H_6 Atten. = x16

volume (ml)	no. of moles ($x10^5$)	average area
0.6	2.68	11280 ± 65.6
0.5	2.23	9360 ± 65.6
0.4	1.78	7624 ± 37.6
0.3	1.34	5616 ± 68
0.2	0.89	3784 ± 37.6

C_3H_8 Atten. = x16	no. of moles ($x10^5$)	average area
0.6	2.68	13240 ± 32.8
0.5	2.23	8716 ± 100
0.4	1.78	9440 ± 112.8
0.3	1.34	6784 ± 229.6
0.2	0.89	4304 ± 68

H_2O Atten. = x16

volume (1)	no. of moles ($x10^5$)	average area
0.5	2.78	7493.2 ± 34
0.4	2.22	5890 ± 30
0.3	1.66	4385 ± 16.6
0.2	1.11	2840 ± 16.3
0.1	0.55	1356.7 ± 9.4

CH_3OH Atten. = x16

volume (1)	no. of moles (x10^5)	average area
0.1	0.25	832.5 ± 23.6
0.2	0.50	1810 ± 14.1
0.3	0.74	2786 ± 73.6
0.4	0.99	3916 ± 28.6
0.5	1.24	4846.7 ± 40
1.0	2.5	9540

CH_3CH_2OH Atten. = x16

volume (1)	no. of moles (x10^5)	average area
0.1	0.17	550
0.2	0.34	1055 ± 63.4
0.3	0.51	1830 ± 24.5
0.4	0.68	2540 ± 53.5
0.5	0.86	3297 ± 46.4

Sensitivities of Calibrated Compounds Relative to CH_4:

Compound	Area units/mol (x10^8)	Relative Sensitivity
C_3H_8	5.079	3.435
CH_3OH	3.82	3.140
C_2H_6	3.765	3.096
CO_2	3.73	3.067
CH_3CH_2OH	3.71	3.049
H_2O	2.66	2.187
CO	2.03	1.670
CH_4	1.216	-

Table 1. Determination of degree of reactant mixing as a function of Vernier metering valve constriction.

Reactor Press = 717 psig (49 atm)

Temp. = 30°C

Flow Rate (NTP) = 33 ml/min 10.3s $(\text{reac. vol.})^{-1}$

Inlet			Outlet			V.C. valve	Degree of mixing	
O_2*	CH_4*	% O_2(i)	O_2*	CH_4*	% O_2(o)	(turns)	(i)/(o)	(o)/(i)
15.6	1180	1.32	120	2652	4.525	0.5	0.292	3.42
47.4	1280	3.7	60.2	1400	4.30	0.75	0.86	1.16
53.4	1200	4.45	150	2220	4.95	1.0	0.90	1.11
56.9	1280	4.45	85	1200	5.2	1.125	0.856	1.20

*G.C. peak areas

(i) = inlet

(o) = outlet

V.C. = Vernier constriction

i.e. number of turns out from fully closed

Table 2. Oxidation of CH_4

Reaction analysis - Dual Flow System. Exit line heater - ON

Run 23 Pressure = 729 psig(49.5 atm) Exit line temp. at GSV = 300°C

T = 456°C %O_2 = 7.0 Flow Rate = 5s(reac. vol)$^{-1}$

	CO	CH_4	CO_2	H_2O	CH_3OH	Total
%total	1.384	55.75	2.058	37.67	4.628	
%Cout*	2.17	87.35	3.22		7.25	
%Coxid.+	17.17		25.47		57.35	
C/N_2	1.114	48.850	1.714		3.009	54.687
O/N_2	0.55		1.714	16.46	1.50	20.220

%Conversion CH_4 = 10.51 %Carbon balance** = 98.42

Degree of mixing

Inlet			Outlet			V.C.	Degree of mixing
O_2	CH_4	%O_2	O_2	CH_4	%O_2	1.25	(o)/(c)
123	1480	8.30	134.5	1620	8.30		1.00

*%Carbon balance arrived at as follows:

$$CB = \frac{\text{output carbon (from reactor)}}{\text{input carbon (to reactor)}} = \frac{{}_i\ C/N_2 \text{ products}}{CH_4/N_2 \text{ reaction}} \times 100$$

Table 3a. Oxidation of CH_4.

Reaction analysis at 50 atm. Reaction zone = 45 cm

Run 24

Pressure = 734 psig (49.9 atm)

T = 451°C

$\%O_2 = 6.7$

Flow Rate = 10s(reac. vol)$^{-1}$

CH_4/N_2 reactants = 56.82

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.436	65.46	2.396	-	14.26	vs$^+$	17.316	
% Cout	1.676	76.36	2.653	-	-	-	19.150	
% Coxid	12.60±0.76		11.42±1.46				76.00 ± 1.41	
C/N_2	1.018	47.25	1.743				11.813	61.824
O/N_2	0.509		1.743		5.13		5.91	13.292

% conversion CH_4 = 9.50 (CH_3OH/H_2O) S.F.* = 0.789

% CH_3OH converted from CH_4 = 7.22 % C balance = 108.8

+notation, s = small, vs = very small, t = trace, will be used throughout these tables

*S.F. = sensitivity factor; i.e., CH_3OH/H_2O ratio multiplied by S.F.

Above determinations made with Exit line heater switched OFF (Temp = 40°C).

Table 3b. Oxidation of CH_4.

Reaction analysis = Variation of CH_3OH yield with Exit line Temperature.

Run 24 cont'd...

1. Exit line temperature (i) (at GSV =) 310°C

(ii) (at capillary temp =) 110°C

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	2.76	72.41	2.55	-	15.05	t	7.32	
% Cout	3.25	85.25	2.87				8.62	
% Coxid.	22.07		19.48				58.44	
C/N_2	1.096	28.71	0.961				2.903	32.71
O/N_2	0.54		0.961		3.0		1.46	5.96

CH_3OH/H_2O S.F. = 0.316

% C balance = 32.71/56.82 = 57.6

2. Exit line temperature (i) 180°C (ii) 50°C

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.36	73.00	2.18	-	18.00	t	5.58	
% Cout	1.66	88.86	2.66				6.81	
% Coxid	14.89		23.93				61.17	
C/N_2	0.875	46.87	1.406				3.59	52.74
O/N_2	0.437		1.406		5.68		1.78	

(CH_3OH/H_2O) S.F. = 0.201

% C balance = 52.74/56.82 = 92.79

Table 4. Oxidation of CH_4.

Reaction analysis at 50 atm. Reaction zone = 45 cm

Run 25

Pressure = 735psig (50 atm)

Temp. = 451°C

%O_2 = 3.5

Flow Rate = 10s (reac. vol)$^{-1}$

CH_4/N_2 reactants = 56.18

	CO	CH_4	CO	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	0.862	68.85	1.39	-	18.49	vs	10.39	
% Cout	1.06	84.47	1.71				12.74	
% Coxid	12.57±3.0		10.71±2.20				76.72±4.80	
C/N_2	0.587	47.02	0.944				7.056	55.61
O/N_2	0.293		0.944		6.523		3.526	

%Conversion CH_4 = 5.90±1.40 (CH_3OH/H_2O) S.F. = 0.365

% CH_3OH from CH_4 = 4.55±1.08 % C balance = 98.98

Table 5. Oxidation of CH_4.

Reaction analysis at 50 atm. Reaction zone = 45 cm

Run 26

Pressure = 734 psig (50 atm)

Temp = 453°C

$\%O_2 = 8.0$

Flow Rate = 10s reac. vol

$CH_4/N_2 = 55.55$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.87	58.35	2.81	-	28.19	s	8.65	
% Cout	2.61	81.08	3.95				12.17	
% Coxid.	23.93±5.56		19.34±2.78				56.70±7.60	
C/N_2	1.338	41.48	3.48				6.28	51.48
O/N_2	0.66		3.48		10.31		3.14	

% Conversion CH_4 = 7.53±1.51

(CH_3OH/H_2O) S.F. = 0.199

% CH_3OH from CH_4 = 4.35±1.37

% C balance = 92.7

Table 6. Oxidation of CH_4.

Reaction analysis at 35 atm. Reaction zone = 45 cm

Run 27

Pressure = 506 psig (34.4 atm)

Temp = 450.5°C

$\%O_2$ = 2.11

Flow Rate = 10s $(\text{reac. vol})^{-1}$

CH_4/N_2 reactants = 55.55

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	0.47	62.82	0.89	-	29.32	s	6.32	
% Cout	0.60	88.77	1.27				9.13	
% Coxid	10.75±4.00		12.27±3.76				76.96±7.40	
C/N_2	0.363	51.00	0.456				4.815	56.634
O/N_2	0.181		0.456		13.02		2.407	

% Conversion CH_4 = 3.90±1.01

(CH_3OH/H_2O) S.F. = 0.138

% CH_3OH from CH_4 = 3.08±1.10

% C balance = 101.9

Table 7. Oxidation of CH_4.

Reaction analysis at 35 atm. Reaction zone = 45 cm

Run 28

Pressure = 511 psig (34.7 atm)

Temp. = 453.4°C

$\%O_2$ = 6.0

Flow Rate = 10s (reac. vol)$^{-1}$

CH_4/N_2 reactants = 52.91

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.72	57.60	2.18	-	27.816	s-vs	10.56	
% Cout	2.40	80.60	3.05				14.35	
% Coxid	20.70±2.87		14.68±3.82				64.60±6.02	
C/N_2	1.318	43.970	1.661				6.79	53.73
O/N_2	0.659		1.661		12.150		3.390	

% Conversion CH_4 = 8.07±1.17

% CH_3OH from CH_4 = 5.28±1.26

(CH_3OH/H_2O) S.F. = 0.24

% C balance = 101.6

Table 8. Oxidation of CH_4.

Reaction analysis at 35 atm.   Reaction zone = 45 cm.

Run 29

Pressure = 499 psig (34 atm)

Temp = 455°C

% O_2 = 10.3

Flow Rate = 10s (reac vol)$^{-1}$

CH_4/N_2 reactants = 54.42

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH
%total	1.88	56.37	2.10	-	30.83	vs	8.73
% Cout	2.73	81.65	3.03				12.49
% Coxid	25.13±3.28		15.09±2.65				59.86±3.44
C/N_2	1.709	51.217	1.893				8.572
O/N_2	0.859		1.893		14.53		4.286

% Conversion CH_4 = 7.51±1.11 (CH_3OH/H_2O) S.F. = 0.184

% CH_3OH from CH_4 = 4.54±1.00   % C balance = 116.5

Table 9. Oxidation of CH_4.

Reaction analysis at 65 atm.

a) Reaction zone = 45 cm.

Run 30 Pressure = 965 psig (65.6 atm) Flow Rate = 10s reac. vol^{-1}

CH_4/N_2 reactants = 54.525 Temp. = 468°C

O_2/N_2 reactants = 1.445 $\%O_2$ = 2.65

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	0.48	81.45	1.01	-	10.28	s	6.33	
% Cout	0.65	91.02	1.13				7.07	
% Coxid	9.57±4.00		8.90±2.30				81.50±6.23	
C/N_2	0.431	57.76	0.719				4.529	63.439
O/N_2	0.215		0.719		3.757		2.264	6.955

% Conversion CH_4 = 5.27±1.75 (CH_3OH/H_2) S.F. = 0.388

% CH_3OH from CH_4 = 4.30±1.75 % C balance = 116.4

(b) Oxidation of CH_4.

Reaction analysis at 65 atm. Reaction zone = 35 cm*.

Conditions same as 9a.

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	0.72	81.02	1.22	-	7.57	s	9.44	
% Cout	0.78	87.65	1.32				10.24	
% Coxid	11.25±1.25		10.50±1.13				78.25±1.65	
C/N_2	0.48	53.55	0.809				6.28	61.12
O/N_2	0.240		0.809				2.631	

% Conversion CH_4 = 4.50±0.50 (CH_3OH/H_2O) S.F. = 0.817

% CH_3OH from CH_4 = 3.50±0.50 % C balance = 112.1

*average of 2 determinations only

Table 10. Oxidation of CH_4.

Run 31 Reaction analysis at 65 atm.

(a) Reaction zone = 45 cm.

Pressure = 960 psig(65.3 atm) Temp = 456°C

$\%O_2$ = 5.15 Flow Rate = 10s (reac. vol)$^{-1}$

CH_4/N_2 reactants = 52.63 O_2/N_2 reactants = 2.724

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.10	71.48	1.23	-	9.94	s	16.08	
% Cout	1.22	79.34	1.35				17.88	
% Coxid	10.70±0.65		6.36±0.54				82.93±0.00	
C/N_2	0.781	50.896	0.876				3.81	56.38
O/N_2	0.390		0.876		3.542		5.710	10.391

% Conversion CH_4 = 7.96±0.76 (CH_3OH/H_2O) S.F. = 1.081

% CH_3OH from CH_4 = 6.61±0.71 % C balance = 107.03

(b) Reaction zone = 35 cm.

Pressure = 963 psig (65.5 atm) Temp. = 463°C

% O_2 = 5.15 Flow Rate = 10s (reac. vol)$^{-1}$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	0.99	71.89	1.17	-	9.71	s	16.10	
% Cout	1.06	77.33	1.29				17.84	
% Coxid	9.41±0.35		6.29±0.15				84.52±0.08	
C/N_2	0.734	54.87	0.894				4.10	60.56
O/N_2	0.367		0.894		3.732		6.142	11.638

% Conversion CH_4 = 7.79±0.37 (CH_3OH/H_2O) S.F. = 1.10

% CH_3OH from CH_4 = 7.00±0.70 % C balance = 115.1

Table 11. Oxidation of CH_4.

(a) Reaction analysis at 65 atm. Reaction zone = 45 cm.

Run 32

Pressure = 962 psig (65.4 atm) Temp = 456°C

$\%O_2 = 7.36$ Flow Rate = 10s (reac. vol)$^{-1}$.

CH_4/N_2 reactants = 53.16 O_2/N_2 reactants = 3.913

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	2.81	67.136	2.53	vs	13.16	s-vs	16.02	
% Cout	3.37	74.38	3.03				18.53	
% Coxid	22.56±6.00		10.90±1.18				66.54±6.30	
C/N_2	1.22	45.79	0.62				3.95	53.60
O/N_2	0.61		0.62		2.77		1.87	5.87

% Conversion CH_4 = 10.98 (CH_3OH/H_2O) S.F. = 0.638

% CH_3OH from CH_4OH = 7.33 %C balance = 98.93±3.80

(b) Reaction zone = 35 cm. Temp = 463°C

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	2.90	54.03	2.18	t	26.43	s	14.84	
% Cout	3.93	73.42	2.98				20.19	
% Coxid	24.30±5.04		10.00±1.85				65.22±4.00	
C/N_2	1.46±0.03	46.35±1.24	0.63±0.31				4.25±1.02	52.68±2.61
O/N_2	1.240		1.882				6.374	20.668

% Conversion CH_4 = 11.73±0.49 (CH_3OH/H_2O) S.F. = 0.365

% CH_3OH from CH_4 = 7.53±0.82 % C balance = 99.10±2.10

Table 11b. Revised (See Appendix IB)

	CH_3OH	
% Cout	6.73±0.53	
% Coxid	65.22±4.00	
C/N_2	4.11±0.33	52.68±2.61

%Conversion CH_4 = 11.73±0.49

%CH_3OH from CH_4 = 7.53±0.82

%C balance = 99.10±2.10

Table 12.

Oxidation of Methane: Variation with Temperature at 65 atm.

Run 33

Pressure = 65 atm

Oxygen concentration = 4.74%

CH_4/N_2 = 50.68

Reactor length = 45 cm

(i) Temp = 455°C

Flow Rate = 5s (reaction vol)$^{-1}$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.11	55.88	0.76	vs	1800	vs	11.58	
% Cout.	1.59	80.59	1.10		30.66		16.71	
% Coxid.	14.44		5.55				80.00	
C/N_2	1.00	50.46	0.692				10.46	62.615
O_2/N_2	0.50		0.692		13.84		5.23	20.240

% conversion CH_4 = 7.60

% C balance = 92.80

% CH_3OH from CH_4 = 6.08

(ii) Temp. = 461°C

Flow Rate = 5s (reac. vol)$^{-1}$

% total	1.27	71.57	1.14	vs	18.54	vs	7.48	
% Cout.	1.56	87.86	1.39				9.18	
% Coxid.	21.76		10.64				67.60	
C/N_2	0.95	53.65	0.85				5.61	61.07
O_2/N_2	0.42		0.85		6.95		2.80	

% conversion CH_4 = 4.70

% C balance = 111.0

% CH_3OH from CH_4 = 3.20

Table 12...cont'd...

Run 33

(iii) Temp. = 477°C Flow Rate = 5s (reac. vol)$^{-1}$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.28	63.87	1.31	vs	24.80	vs	8.73	
% Cout.	1.69	84.93	1.75				11.62	
% Coxid.	19.33		10.84				69.80	
C/N_2	1.01	50.75	1.04				6.94	59.75
O_2/N_2	0.50		1.04		9.85		3.47	

% conversion from CH_4 = 5.86 % C balance = 106.4

% CH_3OH from CH_4 = 4.10

(iv) Temp. = 483°C Flow Rate = 5s (reac. vol)$^{-1}$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.32	71.97	1.05	vs	14.73	-	10.91	
% Cout.	1.55	84.42	1.23				12.80	
% Coxid.	17.10		7.50				75.42	
C/N_2	0.97	52.96	0.77				8.03	62.73
O_2/N_2	0.48		0.77		5.42		4.01	

% conversion from CH_4 = 6.00 % C balance = 111.0

% CH_3OH from CH_4 = 4.52

Table 12 (cont'd...)

Run 33

(v) Temp. = 510°C Flow Rate = 5s (reac. vol)$^{-1}$

	CO	CH_4	CO_2	C_2H_6	H_2O	$(CH_3)_2O$	CH_3OH	Total
% total	1.24	62.34	1.36	vs	20.54	vs	14.52	
% Cout.	1.56	78.54	1.71					
% Coxid.	12.75		7.61				79.64	
C/N_2	0.95	48.00	1.04				11.18	60.18
O_2/N_2	0.47		1.04		7.91		5.60	15.02

% conversion CH_4 = 8.52 % C balance = 103.5

% CH_3OH from CH_4 = 6.78

(vi) Temp. = 515°C Flow Rate = 5s (reac. vol)$^{-1}$

% total	1.32	68.77	1.45	vs	15.74	vs	12.71	
% Cout.	1.56	81.62	1.72				15.09	
% Coxid.	14.84		8.90				76.25	
C/N_2	0.98	51.17	1.08				9.46	62.69
O_2/N_2	0.49		1.08		5.86		4.73	

% Conversion CH_4 = 7.16 % C balance = 108.7

% CH_3OH from CH_4 = 5.46

Table 13. Retention data for Porapak Q, Porapak S, Chromosorb 102 and Carbosieve B.

1. Porapak Q. column conditions. initial temp = 29°C Hold 1 min.
temp rise = 25°C min^{-1} final temp = 125°C

Compound	Air	CO	CH_4	CO_2	C_2H_6	H_2O	C_3H_8	$(CH_3)_2O$	CH_3OH
Rel. Retention	1.00	1.00	1.54	3.07	6.61	8.46	11.92	12.92	14.00

2. Porapak S. column conditions initial temp = 25°C hold 1.5 min
temp rise = 40°C min^{-1} final temp = 180°C

Compound	Air	CO	CH_4	CO_2	C_2H_6	H_2O	C_3H_8	$(CH_3)_2O$	CH_3OH
Rel. Retention	1.00	1.06	1.49	4.26	6.0	10.26	10.26	11.46	12.53

3. Chromosorb 102. column conditions initial temp = 29°C
Hold 1 min. temp rise = 25°C min^{-1}
final temp = 75°C

Compound	Air	CO	CH_4	CO_2	C_2H_6	H_2O	C_3H_8	$(CH_3)_2O$	CH_3OH
Rel. Retention	1.00	1.00	1.5	2.75	7.00	10.12	13.75	15.25	18.75

4. Carbosieve B. column conditions initial temp = 25°C hold 2.5 mins
temp rise = 32°C min^{-1} final temp = 180°C

Compound	O_2	N_2	CO	CH_4	CO_2	C_2H_6	H_2O	C_3H_8	$(CH_3)_2O$	CH_3OH
Rel. Retention	1.00	1.14	-	3.58	-	5.27	5.86	-	-	5.86

Table 14.

Composition of TN-Ngas

cpd.	N_2	CH_4	CO_2	C_2H_6	C_3H_8	C_4 and above
%	0.405	96.40	0.63	1.35	0.73	0.45

Table 15.

Determination of (i) depletion of reactant hydrocarbon in Natural Gas,
(ii) percentage of oxidized yield derived from constituent hydrocarbons.

Reactant hydrocarbon (in Ngas)	C/N_2 ratio in reactant	C/N_2 ratio in product	C/N_2 depletion*	% oxidized yield derived from hydrocarbon
CH_4	229.155	185.60	39.813	94.96
C_2H_6	9.725	8.00	1.577	3.76
C_3H_8	4.285	3.70	0.535	1.28
C_4	3.082	3.360	none when carbon balance allowed for	

*allowing for Carbon balance of 109.4%.

Table 16.

Oxidation of Natural Gas: Variation with Temperature.

Run 34

Pressure = 65 atm | % Oxygen conc. = 3.85%

Hydrocarbon/N_2 = 229.15 | Reaction length = 45 cm

(a) Temp. = 310°C | Flow Rate = 7-20s $(\text{reac. vol})^{-1}$

	O_2	N_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
% total	2.215	0.356	-	63.92	1.53	3.21	2.11	19.69	5.95	
% Cout.			-	8.40	1.95	4.19	2.86		7.38	
% Coxid.			-		*5.08±0.35				94.90±0.35	
C/N_2			-	181.44	4.23	9.06	6.19		15.99	216.91
± std. dev.				6.21	0.14	0.74	0.71		2.36	
O_2/N_2	6.29		-		4.23			29.37	8.00	47.89
± std. dev.	0.21				0.14			4.14	1.18	

% conversion N gas = 2.84±0.27

% C balance = 94.66

% CH_3OH from N gas = 2.62±0.25

Fraction O_2 consumed = 0.23

*% CO_2 produced by reaction

Table 16 (cont'd...).

Oxidation of Natural Gas: Variation with Temperature.

Run 35

Pressure = 65 atm | Oxygen concentration = 5.46%

Hydrocarbon/N_2 = 229.15 | Reactor length = 45 cm

(b) Temp. = 360°C | Flow Rate = 20s $(\text{reac. vol})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_2OH	Total
% total	0.24	0.74	0.69	48.59	2.98	4.20	2.48	25.91	14.17	
% Cout.			0.94	66.45	4.08	5.44	3.39		19.38	
% Coxid.			7.60		9.50				82.92	
C/N_2			2.83	200.0	3.30	8.64	5.10		29.16	249.03
O_2/N_2		3.00	1.41		3.30			53.33	14.58	

% Conversion N gas = 9.63 | % C balance = 107.0

% CH_3OH from N gas = 8.00 | Fraction of O_2 consumed = 0.73

(c) Temp. = 368°C | Flow Rate = 20s $(\text{reac. vol})^{-1}$

% total	0.343	-	1.34	63.74	2.19	2.75	1.27	13.6	14.76	
% Cout.			1.57	74.91	1.43	3.23	1.49		17.35	
% Coxid.			13.62		6.75				79.63	
C/N_2			3.90	185.60	3.55	8.00	3.70		43.00	250.60
O_2/N_2			1.95		3.55			19.80	21.50	

% conversion N gas = 8.30 | % C balance = 95.3

% CH_3OH from N gas = 6.60

Table 17.

Oxidation of Natural Gas: Variation with Temperature.

Run 36

Pressure = 65 atm

Oxygen concentration = 6.93%

Hydrocarbon/N_2 = 229.15

Reactor length = 45 cm

(a) Temp. = 415 °C

Flow Rate = 13s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
% total	0.32	-	2.23	71.45	2.31	2.31	1.60	7.9	11.80	
% Cout.			2.35	75.29	2.43	2.43	1.68		12.43	
% Coxid.			24.90		5.33				69.78	
C/N_2			5.60	179.20	5.80	5.80	4.00		29.60	230.00
O/N_2			2.80		5.80			10.0	14.50	

% conversion N gas = 6.86

% C balance = 100.40

% CH_3OH from N gas = 4.78

(b) Temp. = 420°C

Flow Rate = 12s (reac. vol)$^{-1}$

% total	0.34	-	2.20	66.11	2.55	2.62	1.65	11.84	12.67	
% Cout.			2.51	75.29	2.90	2.98	1.88		14.43	
% Coxid.			23.02		6.71				70.26	
C/N_2			6.40	192.00	7.40	7.60	4.80		36.80	255.00
O_2/N_2			3.20		7.40			17.20	18.40	

% conversion N gas = 7.90

% C balance = 97.17

% CH_3OH from N gas = 5.60

Table 17...cont'd...

Run 36

(c) Temp. = 428°C Flow Rate = 12s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
% total	0.34	-	1.95	64.05	2.55	2.65	2.41	13.69	14.27	
% Cout.			2.30	75.69	3.02	3.13	2.85		16.87	
% Coxid.			19.11		6.50				74.40	
C/N_2			5.77	189.71	7.57	7.86	7.14		42.28	252.47
O_2/N_2			2.88		7.57			20.53	21.14	

% conversion N gas = 8.46 % C balance = 98.2

% CH_3OH from N gas = 6.30

Table 18. Oxidation of Natural Gas Variation with Pressure.

Run 37

Pressure = 50 atm

Temperature = 351°C

Oxygen conc. = 2.6%

Flow Rate = 13s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
% total	0.343	-	0.132	69.86	0.373	3.74	2.00	14.37	9.52	
% Cout.			0.150	81.56	0.436	4.36	2.33		11.14	
% Coxid.			3.40±1.80		4.30±1.78				92.06±3.19	
C/N_2			0.38	203.91	1.09	10.91	5.84		27.91	
±std. dev.			0.87	1.00	0.068	0.31	0.34		2.80	250.04
O_2/N_2			0.19		1.09			21.21	13.95	
± std. dev.			0.043		0.068			5.27	1.40	

% conversion N gas = 4.10±0.54

% C balance = 104.4

% CH_3OH from N gas = 3.77±0.60

Table 19. Oxidation of Natural Gas: Variation with Pressure

Run 38

Pressure = 35 atm

Temperature = 350°C

Oxygen conc. = 2.5%

Flow Rate = 12s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
% total	0.35	1.49	0.37	65.04	1.32	3.46	2.14	20.00	5.82	
% Cout.			0.39	83.09	1.50	4.27	2.49		6.84	
% Coxid.			10.00±1.72		6.94±2.10				83.09±3.53	
C/N_2			1.01	194.81	3.48	9.86	5.86		15.75	230.77
± std. dev.			0.09	7.53	0.19	0.23	0.47		2.08	
O_2/N_2		3.75	0.50		3.48			28.43	7.87	
± std.		0.92	0.04		0.19			-	1.04	

% conversion N gas = 2.96±0.34

% C balance = 95.87

% CH_3OH from Ngas = 2.46±0.35

Fraction of O_2 consumed = 0.36

Table 20. Average composition TN-Ngas* (cf Table 14).

Compound	N_2	CH_4	CO_2	C_2H_6	C_3H_8	C_4
%	0.40	96.16	0.64	1.48	0.72	0.60
±	0.031	1.70	0.03	0.08	0.02	0.24

*determined by g.c.

Table 21. Composition of Medical Air*.

(i)	N_2	O_2
%	78.78	21.22 ± 0.36

(ii) atmospheric air

	N_2	O_2
%	78.70	21.30 ± 0.57

*Determined by gas chromatography.

Table 22. The oxidation of Natural Gas: Variation with Air concentration.

Run 39

Pressure = 50 atm

Temperature = 350°C

Air conc. = 10.42%

Flow Rate = 12s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	4.78	-	0.476	47.16	1.25	3.17	1.78	14.57	11.84	
%Cout.			0.620	78.94	1.56	3.89	2.12		13.01	
%Coxid.			6.21 ± 0.90		2.07 ± 0.77				90.77 ± 1.24	
C/N_2			0.09	12.84	0.254	0.633	0.344		2.14	16.30
±			0.02	1.01	0.015	0.054	0.053		0.47	
O_2/N_2			0.045		0.254			1.53	1.07	2.90
±			0.010		0.015			0.16	0.23	

%Conversion Ngas = 5.05±0.80

%C balance = 96.3±0.93

%CH_3OH converted = 4.69±0.61

Fraction of O_2 consumed = 1.0

Table 23. The oxidation of Natural Gas: Variation with Air concentration.

(a) Run 41 Reactor length = 45 cm

Pressure = 50 atm   Temp. = 350°C   Air conc. = 14.82%

Flow Rate = $17 s (\text{reac. vol})^{-1}$

Reactant O_2/N_2 = 0.27   % reactant O_2 conc. = 3.36

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	13.06	0.70	0.84	62.88	2.46	2.96	1.31	11.61	9.88	
%Cout.			1.05	78.43	3.07	3.68	1.62		12.13	
%Coxid.			13.06±1.82		7.78±1.40				79.16±3.16	
C/N_2			0.065	4.82	0.19	0.230	0.10		0.75	6.148
±			-	0.12	0.01	0.005	0.01		0.11	
O_2/N_2		0.054	0.032		0.19					
±		-	-		0.01					

% Conversion Ngas = 5.72±0.73   %C bal. = 77.3 ± 3.15

% CH_3OH converted = 4.56±0.75   Fraction of O_2 consumed = 0.80

(b) Run 41 Reactor length = 35 cm

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	11.53	1.94	0.285	62.06	1.88	1.65	1.82	15.50	9.62	
%Cout			0.36	78.83	2.41	4.13	2.08		12.24	
%Coxid			3.36±0.27		5.33±1.44				91.20±1.16	
C/N_2			0.0245	5.39	0.164	0.282	0.142		0.84	6.83
±			0.005	0.16	0.008	0.002	0.005		0.03	
O_2/N_2		0.168	0.0122		0.164			1.34	0.42	2.11
±		-	0.002		0.008				0.01	

% Conversion Ngas = 4.95±0.29   % C bal. = 85.85 ± 7.15

% CH_3OH converted = 4.31±0.21   Fraction of O_2 consumed = 0.37

Table 24. The oxidation of Natural gas: Variation with Air concentration.

Run 40

Pressure = 50 atm   Temp. 350°C   Air conc. = 20.62%

Flow Rate = 4s (reac. vol)$^{-1}$ O_2 conc. = 4.36%

Reactant O_2/N_2 = 0.256

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	17.28	2.03	0.87	59.00	2.40	2.67	1.40	13.64	7.72	
%Cout			1.20	80.85	3.32	3.67	1.89		10.01	
%Coxid			16.94±2.76		8.85±3.26				74.46±1.80	
C/N_2			0.05	3.41	0.14	0.154	0.079		0.423	4.26
±				0.11	0.22	0.017	0.012		0.060	
O_2/N_2		0.117	0.025		0.14			0.41	0.211	0.903
±		0.001			0.02			0.04	0.030	

% conversion Ngas = 4.91±0.69   % C bal. = 88.85 ± 2.43

% CH_3OH converted = 3.82±0.63   Fraction of O_2 consumed = 0.55

Table 25. The oxidation of Natural Gas: Glass lined catalytic reactor.

Run 42 Pressure = 50 atm Temp. = 350°C

Flow Rate = 12s(reac. vol)$^{-1}$ O_2 conc. = 5.7%

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	0.25	-	1.01	42.88	1.61	1.74	0.65	31.33	22.06	
%Cout			1.56	61.29	2.35	2.47	0.90		33.12	
%Coxid			7.95±0.56		0.76±0.05				89.65±0.90	
C/N_2			4.25	167.75	6.33	6.76	2.47		90.88	278.44
±			0.04	10.64	0.12	0.48	0.25		7.85	
O_2/N_2			2.12		6.33			63.73	45.44	
±			0.02		0.12			2.89	3.82	

% conversion Ngas = 14.26±1.04 % C bal = 90.18 ± 5.67

% CH_3OH converted = 12.79±1.06

Table 26. The oxidation of Natural Gas: Glass lined reactor

Run 43 Pressure = 30 atm Temp. = 350°C

Flow Rate = 12.1s (reac. vol)$^{-1}$ O_2 conc. = 4.84

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	0.21	-	0.96	36.90	1.40	1.61	0.72	34.75	23.47	
%Cout			1.48	56.41	2.06	2.32	0.84		37.09	
%Coxid			6.93±0.45		1.04±0.38				92.07±0.66	
C/N_2			4.81	183.50	6.71	7.53	2.68		112.68	317.91
±			0.19	3.93	0.19	0.32	0.57		18.08	23.28
O_2/N_2			2.40		6.71			84.34	56.34	
±			0.10		0.19				9.04	

% Conversion Ngas = 13.36±1.77 %C bal = 106.02 ± 5.62

% CH_3OH converted = 12.53±1.51

Table 27. The oxidation of Natural Gas: Silver wall catalyst.

(a) Temp. = 350°C

Run 44

Pressure = 30 atm

O_2 conc. = 5.50 %

Catalyst zone length = 45 cm

Reactant O_2/N_2 = 11.22

Detmn.[+] #1 Flow Rate = 12.6 s(reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								O/S*		
%Cout				87.64	4.66	4.66	2.41		0.62	
%Coxid					80.00				20.00	
C/N_2				216.92	11.53	11.53	5.96		1.56	247.50
O_2/N_2		6.88			5.77				0.78	

% conversion N gas = 1.33

%C bal. = 106.3

% CH_3OH converted = 0.266

Fraction of O_2 consumed = 0.39

[+] Determinations made sequentially. Time interval between determinations approx. 30 min.

*O/S = off scale: Any analysis where water was off scale meant that the percentage area values could not be determined.

Table 27...cont'd...

Detmn. #2 Flow Rate = 12.5s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								O/S		
% Cout			vs	86.16	5.24	4.44	1.98		2.17	
%Coxid			0.55		59.31				40.14	
C/N_2			0.066	193.78	11.77	10.00	4.44		4.88	224.95
O_2/N_2		5.15	0.033		5.88				2.44	13.50

% conversion Ngas = 5.03 %C bal. = 93.08

% CH_3OH converted = 2.02 Fraction of O_2 consumed = 0.54

Detmn. #3 Flow Rate = 15.4s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area	0.31	0.75	0.43	63.61	4.04	3.50	1.80	19.88	5.66	
%Cout			0.55	80.92	5.13	4.44	2.30		7.20	
%Coxid			5.13		27.80				67.04	
C/N_2			1.38	203.07	12.88	11.15	5.77		18.07	252.32
O_2/N_2		2.42	0.69		12.88			31.73	9.03	

% conversion Ngas = 7.24 % C bal. = 105.7

%CH_3OH converted = 4.86 Fraction of O_2 consumed = 0.78

Table 27...cont'd...

Detmn. #4 Flow Rate = 13.3s (reac vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								O/S		
%Cout			vs	85.23	5.27	4.38	2.16		2.95	
%Coxid			0.35		51.13				48.52	
C/N_2			0.05	202.00	12.50	10.37	5.12		7.00	237.04
O_2/N_2		5.45	0.18		12.50				3.50	

% conversion Ngas = 5.97 % C bal. = 98.10

% CH_3OH converted = 2.89 Fraction of O_2 consumed = 0.51

(b) Temp. = 407°C Flow Rate = 14s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								O/S		
%Cout			1.71	65.78	3.40	3.15	1.16		24.79	
%Coxid			6.08		5.71				88.20	
C/N_2			4.93	189.62	9.81	9.07	3.33		71.48	288.26
O_2/N_2			2.41							

% conversion Ngas = 11.25 % C bal. = 123.8

% CH_3OH converted = 9.92 oxygen completely consumed

Table 28. The oxidation of Natural Gas: Copper wall catalyst

Run 45 Pressure = 30 atm O_2 conc. = 4.73%

Catalyst zone length = 45 cm Reactant O_2/N_2 = 11.80

(a) Temp. = 350°C Flow Rate = 9.9s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								o/s		
%Cout				90.275	2.68	4.57	2.34		0.12	
%Coxid					83.35 ± 5.55				16.66 ± 5.55	
C/N_2				216.30	6.43	10.95	5.57		0.29	239.54
±				1.30	0.17	0.45	0.32		0.11	
O_2/N_2		10.55			6.43				0.15	
±		0.05			0.17				0.05	

% conversion N gas = 0.725 ± 0.05 % C bal. = 99.67

% CH_3OH converted = 0.123 ± 0.04 Fraction of O_2 consumed = 0.106

(b) Temp. = 403°C Flow Rate = 10.4s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH	Total
%Area								O/S		
%Cout			1.00	78.78	0.65	1.01	0.34		18.26	
%Coxid			4.77		3.27				91.95	
C/N_2			2.20	183.11	2.90	2.35	0.81		42.40	233.8
O_2/N_2			1.83		8.88				66.66	

% conversion Ngas = 9.30 %C bal. = 103.6

% CH_3OH converted = 8.55 Oxygen completely consumed

Table 29. Reaction Analysis of Oxidation of TN-Ngas over various catalysts. Temperature of non catalytic section of glass inserts was maintained at 300°C, i.e. below reaction temperature unless otherwise stated.

Pressure = 30 atm RFR - kept as close to 10s (reac. vol)$^{-1}$ as possible.

Catalyst	Run #	Reactant O_2 conc. (%)	Product O_2 conc. (%)	Catalyst Temp (°C)	% yields			%N gas conversion
					CO	CO_2	CH_3OH	
a. Wall catalysts								
Ag	44	5.50	2.67	352	0.35	51.13	48.52	5.97
		5.50	-	400	6.08	5.71	88.20	11.25
Cu	45	4.73	4.21	353	-	88.89	11.11	0.72
		4.73	-	403	2.20	3.27	91.95	14.59
b. Packed catalysts								
10% Cu	46	3.90	-	357	1.88	2.34	95.77	8.37
on SiO_2		3.90	3.90	300	no reaction			
10% Co	47	4.82	3.40	296	-	100	-	1.93
on Al_2O_3		4.82	-		-	100	-	3.37
Hopcalite	48	5.93	3.85	300	-	100	-	1.65
		5.93	-	255	34.20	65.80	-	
		5.93	5.22	210	no reaction			
TiO_2	49	4.03	3.16	303	50.00	50.00	-	1.00
		4.03	1.66	350	50.00	50.00	-	1.76
		4.03	1.00	386	46.87	53.12	-	2.46
		4.03	-	407	56.27	43.72	-	2.35

Table 30. The Oxidation of Natural Gas: Teflon Lined Reactor

Run 50

Pressure = 30 atm Temp. = 350°C

Flow Rate = 9.6s(reac vol)$^{-1}$ NTP O_2 conc. = 4.9%

Space Time (S.T.(reactor)) = 138 s (reac. vol)$^{-1}$;

(30 atm, 357°C)

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area		-						O/S	
% Cout			1.65	56.52	2.20	2.38	0.89		29.46
% Coxid			5.30 ± 0.93		3.60 ± 0.92				9.11 ± 1.85
C/N_2			5.37		7.13	3.57	2.88		94.97
±			0.17		0.40	0.45	0.02		16.20
O_2/N_2			2.67		7.13	3.57			47.47
±			0.08		0.40	0.45			8.10

%conversion N gas = 10.79 ± 2.07

% C bal = 131.9

% CH_3OH converted = 10.03 ± 1.76

Table 31. The Oxidation of Natural Gas: Sb Doped SnO_2 Catalyst.

Run 51

Pressure = 28 atm

Temp. = 307°C

Flow Rate = 10 s(reac. vol.)$^{-1}$ NTP

O_2 conc. = 5.90%

S.T.(reactor) = 146 s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.36	2.86	0.53	68.57	1.96	2.95	1.78	19.28	1.69
% Cout			0.69	88.48	2.53	3.80	2.30		2.20
% Coxid			19.35		19.35				61.30
C/N_2			1.50	192.00	5.50	8.25	5.00		4.75
O_2/N_2		8.00						27.00	

% conversion Ngas = 2.90

% C bal = 100.80

% CH_3OH converted = 1.78

Fraction of O_2 conc. consumed = 0.34

Table 32. Oxidation of Natural Gas: Stainless Steel Wall

Run 52.

Pressure = 30 atm T = 350°C

Flow Rate = 26s (reac. vol)$^{-1}$ NTP O_2 conc. = 7.0%

S.T. (reactor) = 371s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.35	3.73	0.43	80.27	0.69	1.21	0.35	10.38	1.14
% Cout			0.50	93.85	0.85	1.41	0.41		1.33
% Coxid			24.60		10.10				65.30
C/N_2			1.20	226.00	1.96	3.40	1.01		3.18
O_2/N_2		10.50						14.60	

% conversion Ngas = 2.06

% C bal = 105.70

% CH_3OH converted = 1.34

Fraction of O_2 conc. consumed = 0.27

Table 33. Oxidation Ngas: Stainless Steel Reactor.

Run 53.

Pressure = 28.5 atm

Temp. = 379°C

Flow Rate = 32s $(\text{reac. vol.})^{-1}$

O_2 conc. = 7.0%

S.T.(reactor) = 441s $(\text{reac. vol.})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			1.53	79.74	1.42	0.98	0.46		15.85
% Coxid			10.57 ± 0.68		4.92 ± 0.01				84.50 ± 0.70
C/N_2			3.65	188.81	3.39	2.43	1.08		29.15
±			0.64	0.81	0.30	0.02	0.16		0.86
O_2/N_2		-	1.82		3.39			N.D.	14.57
±		-	0.32		0.30			N.D.	0.43

% conversion Ngas = 15.09 ± 0.50

% Cbal = 102.00 ± 0.35

% CH_3OH converted = 12.75 ± 0.12

Table 34. Reaction analysis of oxidation of Ngas over various wall and packed catalysts. (Complete summary)

a. Wall catalysts Pressure = 30 atm Flow Rate = $10 s(\text{reac. vol.})^{-1}$

Run # conc.	Reactant O_2 (%)	Product O_2 conc. (%)	Catalyst Temp. (°C)	% Yields CO	CO_2	CH_3OH	%Ngas conversion
Run 43	4.84	-	Glass(pyrex)350	6.93	1.0	92.07	13.36
Run 44	5.50	2.67	Ag 352	0.35	51.13	48.52	5.97
	5.50	-	Ag 400	6.08	5.71	88.20	11.25
Run 45	4.73	4.21	Cu 353	-	88.89	11.11	0.72
	4.73	-	Cu 403	4.77	3.27	91.95	14.59
Run 50	4.9	-	Teflon 359	5.30	3.60	91.11	10.79
Run 52	7.0	5.14	Stain. St.350	24.60	10.10	65.30	2.06
Run 53	7.0	-	Stain. St.379	10.57	4.92	84.50	15.10
b. Packed catalysts							
Run 46	3.90	3.90	Cu/SiO_2 300		no reaction		
	3.90	-	Cu/SiO_2 357	1.88	2.34	95.77	8.37
Run 47	4.82	3.40	$Co/Al_2O_3$296	-	100	-	1.93
	4.82	-	$Co/Al_2O_3$359	-	100	-	3.37
Run 48	5.93	5.22	Hopcalite 210		no reaction		
	5.93	-	Hopcalite 255	34.20	65.80	-	
	5.93	3.85	Hopcalite 300	-	100	0	1.65

Run #	Reactant O_2	Product O_2	Catalyst		% Yields		%Ngas
	conc.(%)	conc.(%)	Temp.(°C)	CO	CO_2	CH_3OH	Conversion
Run 49	4.03	3.16	TiO_2 303	50.00	50.00	-	1.00
	4.03	1.66	TiO_2 350	50.00	50.00		1,76
	4.03	1.00	TiO_2 386	46.87	53.12		2.46
	4.03	-	TiO_2 407	56.27	43.72		2.35
Run 51	5.90	3.90	Sb/SnO_2 307	31.03	16.90	52.10	1.45

Table 35. Oxidation of Ngas: At 10 atmospheres, variation with temperature.

Run 54.

Pressure = 10.5 atm — Temp. = 356°C

Flow Rate = 10.7 s (reac. vol.)$^{-1}$ NTP — O_2 conc. = 4.22%*

S.T. (reactor) = 53.6 s (reac. vol.)$^{-1}$

O_2 not completely consumed*

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.39	0.26	0.14	72.25	1.56	3.67	1.72	13.33	5.58
% Cout			0.19	84.63	1.74	4.06	2.00		6.50
% Coxid			4.00 ± 1.44		2.03 ± 0.93				93.28 ± 2.27
C/N_2			0.36	181.15	1.88	9.60	4.50		6.23
±			0.08	6.01	0.31	0.56	0.41		1.35
O_2/N_2		0.67	0.18		1.88			17.44	3.12
±		0.33	0.04		0.31			0.56	0.70

%Ngas conversion = 3.27 ± 0.68

%C bal = 97.70

%CH_3OH converted = 3.04 ± 0.69

*See Results and Discussion (Part V, p. 40)

Table 36. Oxidation of Ngas: At 10 atmospheres, variation with temperature.

Run 55.

Pressure = 10.5 atm

Temp. = 411°C

Flow Rate = 11.5s $(\text{reac. vol.})^{-1}$ NTP

O_2 conc. % = 4.22*

S.T. (reactor) = 57.4 s $(\text{reac. vol.})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.39		0.05	86.62	-	1.59	0.75	8.07	2.60
% Cout			0.06	94.62		1.74	0.82		2.84
% Coxid			2.03						97.97
C/N_2			0.140	221.31		4.07	1.92		6.65
O_2/N_2		-	0.07					10.37	3.32

% conversion Ngas = 3.47

% C bal = 119.0

% CH_3OH converted = 3.40

*See Results and Discussion (Part V, p. 40).

Table 37. Oxidation of Ngas. At 10 atmospheres, variation with flow rate.

Run 56.

Pressure = 9.8 atm

Temp. = 356°C

Flow Rate = 11.3s (reac. vol.)$^{-1}$ NTP

O_2 conc. = 7.22%

S.T. (reactor) = 52.6s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.53	6.10	-	80.14	-	1.56	0.70	9.82	1.15
%Cout				95.92		1.86	0.84		1.38
%Coxid			-						100
C/N_2				152.00		2.95	1.33		218
O_2/N_2		11.57							

% conversion Ngas = 1.33

% C bal = 96.70

% CH_3OH converted = 1.33

Fraction of O_2 conc. consumed = 0.08

Table 38. Oxidation of Ngas: At 10 atmospheres, variation with flow rate.

Run 57.

Pressure = 11.0 atm Temp. = 387°C

Flow Rate = 14.6s (reac. vol.)$^{-1}$ NTP O_2 conc. = 7.10%

S.T. (reactor) = 72.6s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			1.03	83.49	0.21	0.94	0.43		13.62
% Coxid			6.97 ± 0.94		1.53 ± 0.35				91.49 ± 0.90
C/N_2			1.90	149.71	0.38	2.17	0.77		25.03
±			0.76	0.93	0.06	0.17	0.14		10.37
O_2/N_2		6.74	0.85		0.38				12.51
±		2.04	0.38		0.06				5.14

% conversion Ngas = 6.36 ± 0.71

% C bal = 109.5

% CH_3OH converted = 6.00 ± 0.79

Fraction of O_2 conc. consumed = 0.45

Table 39. Oxidation of Ngas: At 10 atm variation with flow rates.

Run 58.

Pressure = 9.3 atm

Temp. 374°C

Flow Rate = 27s (reac. vol.)$^{-1}$ NTP

O_2 conc. = 4.5%

S.T. (reactor) = 117s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.27	-	1.12	51.36	0.02	0.06	0.17	37.28	9.24
% Cout			1.48	78.45	0.30	1.07	0.35		18.34
% Coxid			7.62 ± 2.15		1.54 ± 0.42				90.83 ± 2.48
% C/N_2			3.33	173.62	0.66	2.36	0.76		40.82
±			0.70	12.13	0.08	0.12	0.10		8.97
%O_2/N_2			1.66		0.66				20.41
±			0.35		0.08				4.00

%conversion Ngas = 7.23 ± 0.90

% C bal = 113.6

% CH_3OH converted = 6.55 ± 1.0

O_2 completely consumed

Table 40. Oxidation of Ngas. At atmospheric pressure. Variation with temperature (glass lined Reactor).

Run 59.

(a) Pressure = 1 atm Temp. = 350°C

Flow Rate = 128.6s (reac. vol.)$^{-1}$ NTP O_2 conc. = 10.31%

S.T. (reactor) = 103s (reac. vol.)$^{-1}$ O_2 conc. cons. = none

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.47	10.79	-	80.58	-	1.35	0.55	6.25	-
% Cout			-	37.70	-	1.63	0.66		-

% Coxid No reaction

(b) Pressure = 1 atm Temp. = 377°C

Remaining parameters as a) S.T.(reactor) = 98.7s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.49	10.42	-	81.75	-	1.50	0.73	5.11	-
% Cout			-	97.34	-	1.78	0.87		-

% Coxid No reaction

Table 40...cont'd...

(c) Pressure = 1 atm　　　Temp. = 400°C

Flow Rate = 148.1 (reac. vol.)$^{-1}$ NTP　　　S.T. (reactor) = 110.20s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.57	8.60	-	83.18	-	1.45	0.60	5.60	-
% Cout			-	97.60	-	1.70	0.70		-
%C oxid	No reaction, although O_2 concentration decreased								

(d) Pressure = 1 atm　　　Temp. = 439°C

Flow Rate as c)　　　S.T. (reactor) = 104.15s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			1.98	91.84	0.24	1.64	0.71		10.02
% Coxid			25.78		5.13				69.10
C/N_2			1.86	148.60	0.37	2.57	1.14		5.00
O_2/N_2		14.17	0.93		0.37				2.50

% conversion Ngas = 4.17

% C bal = 91.6

% CH_3OH converted = 2.88

Fraction of O_2 conc. consumed = 0.40

Table 40...cont'd

(e) Pressure = 1 atm Temp. = 457°C

Flow Rate = 158.1 (reac. vol)$^{-1}$ O_2 conc. = 10.31%

S.T. (reactor) = 108s (reac. vol)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.52	6.85	1.10	81.66	0.27	1.32	0.51	5.77	1.95
% Cout			1.32	94.00	0.31	1.52	0.60		2.24
% Oxid			34.00		8.10				57.90
C/N_2			2.20	157.14	0.52	2.54	1.00		3.75
O_2/N_2		13.20	1.10		0.52			5.55	1.88

% conversion Ngas = 5.70

% C bal = 96.3

% CH_3OH converted = 3.30

Fraction of O_2 conc. consumed = 0.45

Table 40...cont'd

(f) Pressure = 1 atm Temp. 490°C

Flow Rate as e). S.T. (reactor) = 106.3s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			4.07	90.65	0.60	1.14	0.51		6.52
% Coxid			36.40		5.40				58.25
C/N_2			6.24	138.86	0.92	1.75	0.79		10.00
O_2/N_2			3.14		0.92				5.00

% conversion Ngas = 15.36

% C bal = 91.4

% CH_3OH converted = 8.95

O_2 completely consumed

Table 40...cont'd

(g) P = 1 atm Temp. = 502°C

Flow Rate as e). S.T. (reactor) = 101.7s $(\text{reac. vol.})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.46	-	3.10	70.26	0.38	0.64	0.24	22.45	3.01
% Cout			4.00	90.76	0.49	0.83	0.31		3.90
% Coxid			47.76		5.83				46.40
C/N_2			6.67	151.42	0.81	1.38	0.52		6.48
O_2/N_2			3.33		0.81			27.43	

% conversion Ngas = 11.63

% C bal = 96.4

% CH_3OH converted = 5.40

O_2 completely consumed

Table 41. Oxidation of Ngas. At atmospheric pressure and 477/457°C.

Run 60

(a) Pressure 1 atm Temp. = 477°C

Flow Rate = 163.6 $(\text{reac. vol.})^{-1}$ NTP O_2 conc. = 10.7%

S.T. (reactor) = 119s $(\text{reac. vol})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			3.34	91.33	0.60	0.86	0.35		3.53
% Coxid			45.00		7.76				47.34
C/N_2			5.39	147.14	0.93	1.38	0.57		5.68
O_2/N_2		4.82	2.69		0.93				2.84

% conversion Ngas = 14.07 % C bal = 92.8

% CH_3OH converted = 3.27 Fraction of O_2 conc. consumed = 0.73

(b) Pressure = 1 atm Temp. = 457°C

Flow Rate and O_2 conc. as a) S.T.(reac) = 122.3s $(\text{reac. vol})^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area								O/S	
% Cout			1.49	87.68	0.33	1.22	0.54		8.72
% Coxid			14.10		3.17				82.73
C/N_2			2.50	146.28	0.56	2.03	0.91		14.56
O_2/N_2		4.50	1.25		0.56				7.28

% Ngas conversion = 14.00 % C bal = 95.0

% CH_3OH converted = 11.60 Fraction of O_2 conc. consumed = 0.77

Table 42. Oxidation of Ngas. Recirculation I.

Run 61 Time of Analysis 11:15

Initial conditions: Pressure = 32.5 atm Temp. = 356°C

Flow Rate = 11.1 s (reac. vol.)$^{-1}$ O_2 conc. = 2.70%

S.T. (reactor) = 171s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Area	0.45	-	0.68	85.40	-	1.12	0.53	6.46	5.36
% Cout			0.73	91.74	-	1.21	0.56		5.76
% Coxid			11.20		-				88.79
C/N_2			1.50	189.33	-	2.50	1.20		11.89
O_2/N_2		-	0.75		-			7.15	6.00

% conversion Ngas = 6.83

% C bal = 105.4

% CH_3OH converted = 6.07

Table 43. Sample analysis of Recycle Gas. (Recirculation I)

(a) O_2, Products, Scrubbers

1. Analysis for oxygen. Time = 13:00

0.8 ml sample from valve S1 (Reactor)

Cpd	N_2	O_2	CO	
%	29	-	71	no O_2 detected

2. 1 ml sample from valve S2 (post condenser) Time = 13:15

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area				O/S				O/S	high
%Coxid			8.36		1.83				89.20

-methanol and water were not being effectively removed

3. 0.8 ml sample from valve S3 (post CO, CO_2 scrubbers) Time = 13:40

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.43	-	0.60	80.60	-	1.05	0.20	13.21	3.91

-CO_2 removed but not CO

-Estimate efficiency of CO removal = 15%

Table 43...cont'd... Analysis of condenser contents (Recirculation I).

(b) Liquid, NMR

Recycle system pressurized; Recirculation commenced at 15:20
Recirculation stopped at 16:30

1. Volume liquid product 1 ml. Duration of recycle - 1 hr 10 min

G.C. 0.2 1 liquid sample direct from condenser

Compound	HCHO	H_2O	CH_3OH	CH_3OH/H_2O
Area	2.30	1040	820	
corr. Area		475.5	261.1	
%Area				0.55
Rt.	7m 54s	10m 36s	12m 42s	

- identification of HCHO not confirmed

2. NMR

Spectrum showed presence of H_2O, CH_3OH and suggested HCHO or hydrated HCHO.

Compound	HCHO	H_2O	CH_3OH
ppm	3.75	5	3.25

3. Mass Spectrometry

Complicated spectrum

Table 44. Oxidation of Ngas Recirculation II.

Run 62. Time of Analysis = 11:35

Initial conditions:

Pressure = 31 atm Temp. = 353°C

Flow Rate = 9.4s (reac. vol.)$^{-1}$ NTP O_2 conc. = 5.05%

S.T. (reactor) = 138s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.51		1.26	81.26	0.45	1.21	0.22	10.30	4.40
%Cout			1.42	91.54	0.51	1.36	0.24		4.94
%Coxid			20.70		7.37				71.94
C/N_2			2.48	160.00	0.88	2.38	0.42		8.64
O_2/N_2			1.24		0.44			10.13	4.32

% conversion Ngas = 7.03*

% C bal = 102.5

% CH_3OH converted = 5.06

---

*See Results and Discussion (Part V, p. 43).

Table 45. Sample Analysis of Recycle Gas. (Recirculation II)

Reaction products admitted to Recycle system at 13:40

1. Analysis for Oxygen

Samples from valve S1. Time = 14:00

Compound	N_2	O_2	CO	
%	16.35	-	83.64	No oxygen
±	1.33		1.33	

2. Analysis for CO, CO_2

Sample from valve S3 (post CO, CO_2 scrubbers) CO_2 completely removed. CO-60% removed.

Table 46. Analysis of Condenser Contents and Recycle Gas (Recycle II).

Recycle system pressurized/Recirculation commenced at 16:00

Recirculation stopped at 22:00

Volume of liquid product = 3 ml   Duration of recycle = 6 hrs

1. G.C. analysis of condenser contents.

a) Headspace; Cylinder pressure = 200 psig (13.6 atm)

Temp. = -30°C

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.49	-	1.10	82.26	0.28	1.20	0.45	9.01	5.20
%Cout			1.21	90.10	0.30	1.33	0.50		5.75
%Coxid			16.70		4.20				79.10
C/N_2			2.28	166.86	0.56	2.44	0.91		10.55
O_2/N_2			1.14		0.56			9.14	5.28

% conversion Ngas = 7.61

% C bal = 103.9

% CH_3OH converted = 6.02

Table 46...cont'd

b) Liquid fraction

0.2 μl of liquid fraction injected

Compound	HCHO	H_2O	CH_3OH	CH_3OH/H_2O
%total	3.52	55.00	41.46	75.38
±	0.36	1.57	1.65	
Rt.	2.45	5.12	7.09	

-identity of HCHO confirmed by calibrating with known mixture as follows:

	HCHO	H_2O	CH_3OH
approx. proportion	1	2	1
by volume	2:45	5:06	7:06

^{1}H NMR

Compound	HCHO	H_2O	CH_3OH
ppm	4.85	5.10	3.65

^{13}CMR

-confirmed presence of HCHO

Table 46...cont'd

2. Analysis of stored recycle gas

Storage cylinder pressure = 750 psig (51 atm)

Temp. = 25°C

0.8 ml sample analysed

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
% Cout			0.51	92.24	-	2.06	1.00		4.18

-CO reduced by 61% over that produced by reaction

-CO_2 completely removed

-H_2O and CH_3OH present in substantial amounts

Table 47. Oxidation of Ngas. Recirculation III

Run 63 Time of analysis = 11:45 (March 12th)

Initial conditions:

Pressure = 29.4 atm Temp. = 350°C

Flow Rate = 12.3s(reac. vol.)$^{-1}$ O_2 conc. = 4.2%

S.T. (reactor) = 176s (reac. vol.)$^{-1}$

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.44	-	0.80	77.38	0.21	1.12	0.39	13.66	6.00
%Cout			0.93	90.10	0.24	1.31	0.46		6.96
%Coxid			11.46		3.00				85.55
C/N_2			1.76	170.00	0.46	2.47	0.86		13.13
O_2/N_2			0.88		0.46				6.56

% conversion Ngas = 8.07

% C bal = 99.2

% CH_3OH converted = 6.90

Table 48. Analysis of Recirculator Gas (Recycle III) after 6 hours.

Reaction products admitted to Recycle system at 13:00 (March 12th)

1. Analysis for oxygen Time = 17:30

Sample from valve S1

Compound	N_2	O_2	CO	
%	37.10	-	62.90	Oxygen not detected

2. Analysis for CO Time = 19:00

Sample from valve S3

Compound	N_2	O_2	CO	CH_4
%	D	N.D.	N.D.	D

D = detected

ND = not detected

Recycle system pressurized/Recirculation commenced at 16:55 (March 12th)

Table 49. Analysis of reaction mixture (Recycle III) after 24 hours operation.

Run 63 cont'd Time of Analysis = 12:30 (March 13th)

Pressure = 34 atm Temp. = 375°C

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.59	-	0.76	88.16	0.11	1.06	0.10	9.24	3.08
%Cout			0.84	94.53	0.12	1.17	0.11		3.30
%Coxid			19.18		2.78				78.04
C/N_2			1.29	149.71	0.18	1.80	0.16		5.23
O_2/N_2			0.62		0.18			7.84	2.61

% conversion Ngas = 6.17

% C bal = 100.80

% CH_3OH converted = 4.82

N_2/CH_4 = 0.61

Table 50. Determination of N_2 concentration at end of Recycle III.

Recirculation stopped at 14:00 (March 14th)

Sample	Compound	N_2	O_2	CO	CH_4	N_2/CH_4
1.0 ml	%	0.69	-	0.95	98.35	0.70
0.8 ml	%	0.60	-	0.83	98.56	0.61

Table 51. Determination of post condenser gas at end of Recycle III.

Pressure = 275 psig (18.7 atm) Temp. = 26°C

	N_2	O_2	CO	CH_4	CO_4	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.65	-	0.85	85.68	0.32	0.80		10.62	1.06
%Cout			0.96	96.57	0.36	0.91			1.19

Concentration of methanol in post condenser gas ~1% but water high at 10%.

Table 52. Analysis of Recycle Gas and Condenser Contents.

a) Recycle gas. Pressure recycle gas storage cylinder = 500 psig (34 atm)

	N_2	O_2	CO	CH_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area	0.52	-	-	86.41	vs	0.50	vs	10.44	2.12
%Cout				97.05		0.56			2.38

-CO and CO_2 removed by scrubbers

-100% efficient throughout experiment

b) Condenser gas - Headspace

Pressure = 240 psig (16.33 atm)

	N_2	O_2	CO	C_4	CO_2	C_2H_6	C_3H_8	H_2O	CH_3OH
%Area			0.74	87.24	0.21	0.56	0.19	10.19	0.84
%Cout			0.83	97.10	0.24	0.62	0.21		0.94

Table 52...cont'd

Recirculation commenced at 16:00 (March 12th), stopped at 14:00 (March 14th)

c) Liquid fraction

Volume collected = 30 ml

Duration of recycle = 46 hours

Compound	HCHO	H_2O	CH_3OH	CH_3OH/H_2O
%	2.82	48.67	48.51	99.67
±	0.58	0.33	0.88	
Rt	2:24	4:21	5:57	

Calibration sample

	HCHO	H_2O	CH_3OH
proportion by vol (approx.)	1	1	0.5
Rt	2:24	4:27	6:09

d) Spectrophotometric determination of HCHO (Parasaniline method).

0.082 ppm contained in 10 ml diluted sample.

Sample fold of dilution = 6.25×10^5

Total concentration of HCHO = 51.250 ppm

= 5.125%

```
                                                                                    MAIL TO:        PAGE      1
                                 MONTHLY   GRANT   REPORT    SIGNING AUTH: CHOW  A.           CLARK  I.B.
THE UNIVERSITY OF MANITOBA                                   DEPARTMENT:   NSERC CRD-8510     CHEMISTRY
GL735        APRIL  9, 1987                                          ACCOUNT NO:    311-1722-10
                                 MAR PRE 1987

                                                           CURRENT        YEAR-TO-DATE
POS                                                   AUTHORIZED   EXPENDITURES   EXPENDITURES    COMMITMENTS     AVAILABLE
 #  SOURCE C REF.NO  NAME OR SOURCE   EMP.NO CDE

GRANT EXPENDITURES
                                          100    37,513.45
           4     BAL MAR 31 1986          100       308.53
     055026 4    FUNDS AUTHORIZED         100    46,000.00
     125176 4    FUNDS AUTHORIZED


                                                                                       14,999.99
SPEC. ACAD. SALARIES                                         1,666.67    18,333.37        34.56
                                          191                  343.12     6,948.44        40.66
          492496 KANTIPULY                170                  410.44     7,453.34    15,075.21
          494252 KATRAGADDA               170                2,420.23    32,735.15
          547018 LEBLANC
                                                             2,420.23    32,735.15    15,075.21
   ** TOTAL SALARIES

 GENERAL STAFF BENEFITS

                                                                                        1,349.99
  STAFF BENEFITS                          300                  187.02                   1,349.99
   035004 6           STAFF BENEFITS      300                  187.02     1,748.23
   035002 3 PAYROL    STAFF BENEFITS EX   300
                      STAFF BENEFITS --                        187.02     1,748.23      1,349.99

                                                               187.02     1,748.23      1,349.99

   ** TOTAL STAFF BENEFITS                                   2,607.25    34,483.38     16,425.20

  ** TOTAL SALARIES & STAFF BEN.

                                                                                          224.99
 PAY LEVY (RESEARCH)                      397
                                          397                   25.00                     224.99
   035005 6           PAY TAX LEVY        397                   25.00       275.00
   035003 3 PAYROL    PROV. PAYROLL LEV   397
                      PAY LEVY (RESEARC                                     740.00
 TRAVEL-ACADEMIC ----------------------------400-
                                                                          1,044.65
 MOVING ALLOWANCE ---------------------------415-

 GEN SUPP AND EXPENSE                     600                   14.52
                                          600                  215.70                     318.00
    66681   1 F38168 MANDEL SCIENTIFIC    600                                             111.51
    66681   1 F38168 MANDEL SCIENTIFIC    600
            6 F38168 MANDEL SCIENTIFIC    600                   98.57
            6 F39952 CHEMI CROWN          600
   035052   3 M41544 CHEMISTRY
```

Table 53b

```
|-------------------------------------------------------------------|
   2     2     2     2     2     2     2     2     2     2     2
|-------------------------------------------------------------------|

FOR EXPERIMENT #25.00
NATURAL GAS FEEDRATE OF  1000000.0 SCF/DAY
MAXIMUM MOLE FRACTION NITROGEN IN REACTANTS OF 0.160
REACTOR PRESSURE OF 735.0 PSIA, TEMPERATURE OF 451.0 DEGREES C
CH4 CONVERSION= 15.280 %   SELECTIVITY= 81.660 %
REACTION BALANCE BASED ON CO2:CO MOLAR RATIO OF      1.613

PROCESS STREAM VALUES ARE TABLED BELOW (ARRAY S(I,J)):
I REFERS TO STREAM NUMBER OF PROCESS FLOWSHEET
P=PSIA, T=DEGREES C, OTHER COLUMNS ARE MOLAR FLOWS (GMOL/SEC)
STEADY STATE ACHIEVED AFTER  76 ITERATIONS:

 I   P   T    CH4     O2     N2      CO      CO2    H2O   CH3OH  TOTAL
------------------------------------------------------------------------
 1 735 451 85.622  9.681 18.598  0.0    0.0    0.0    0.0  116.292
------------------------------------------------------------------------
 2 735 451 72.539  0.0   18.598  0.918  1.481  0.0    0.0  109.019
------------------------------------------------------------------------
 3 725  41 72.539  0.0   18.598  0.918  1.481  0.0    0.0  109.019
------------------------------------------------------------------------
 4 719  41 72.539  0.0   18.598  0.918  1.481  0.0    0.0   93.536
------------------------------------------------------------------------
 5 719  41  0.0    0.0    0.0    0.0    0.0    0.0    0.0   15.482
------------------------------------------------------------------------
 6  14  64  0.0    0.0    0.0    0.0    0.0    0.0    0.0   10.772
------------------------------------------------------------------------
 7  16 105  0.0    0.0    0.0    0.0    0.0    0.0    0.0    4.711
------------------------------------------------------------------------
 8 755  45 72.539  0.0   18.598  0.918  1.481  0.0    0.0   93.536
------------------------------------------------------------------------
 9 755  45  0.259  0.0    0.066  0.003  0.005  0.0    0.0    0.334
------------------------------------------------------------------------
10 755  45 72.280  0.0   18.532  0.915  1.476  0.0    0.0   93.202
------------------------------------------------------------------------
11 753  30 72.280  0.0   18.532  0.0    2.391  0.0    0.0   93.202
------------------------------------------------------------------------
12 753  30 72.280  0.0   18.532  0.0    0.0    0.0    0.0   93.202
------------------------------------------------------------------------
13 753  30 72.280  0.0   18.532  0.0    0.0    0.0    0.0   93.202
------------------------------------------------------------------------
14 735  25 13.336  0.0    0.067  0.0    0.0    0.0    0.0   13.403
------------------------------------------------------------------------
15 735  25  0.0    9.681  0.0    0.0    0.0    0.0    0.0    9.681
------------------------------------------------------------------------
16 735  25 85.622  9.681 18.598  0.0    0.0    0.0    0.0  116.292
------------------------------------------------------------------------
```

```
FOR EXPERIMENT # 25.0
T H E R M A L   A N A L Y S I S
-------------------------------

E N E R G Y   I N P U T S :
HEAT VALUE OF GAS FEED =    2557263.0 CAL/SEC
COMPRESSOR WORK IN =           4554.3 CAL/SEC
(PUMPING WORK IS NEGLECTED)

U S E F U L   E N E R G Y   O U T P U T :
EXCESS REACTOR HEAT OF             503878.4 CAL/SEC AT 451.0C
METHANOL HEAT VALUE OF            1630223.0 CAL/SEC
PURGE FLOW HEAT VALUE OF            49883.9 CAL/SEC

L O W   G R A D E   E N E R G Y   O U T P U T :
CO CONVERTER HEAT OF ,              74587.3 CAL/SEC AT 30.0C
OVERHEAD CONDENSOR HEAT OF         200185.7 CAL/SEC AT 64.5C
BOTTOMS WATER FLOW OF                  1.12 IGPM AT 105.0C
(  216281.7 CAL/SEC WERE USED TO DRIVE DISTILLATION)
THERMODYNAMIC EFFICIENCY=USEFUL ENERGY OUTPUT / ENERGY INPUT * 100
EFFICIENCY = 2183984.0/2561817.0 *100 =      85.3 %
                                          ---------

C O S T   A N A L Y S I S
-------------------------

EQUIPMENT UNIT                 SIZE          COST         COST PER LITRE
--------------                 ----          ----         --------------
REACTOR                  32121.4 FT**2    $716954.50      $0.0073/LITRE
PREHEATER                 5891.5 FT**2    $141334.12      $0.0014/LITRE
DISTILLATION CONDENSOR     458.6 FT**2    $ 13738.93      $0.0001/LITRE
DISTILLATION REBOILER      318.2 FT**2    $ 11824.80      $0.0001/LITRE
CO CONVERTER COOLER        359.9 FT**2    $ 20175.90      $0.0002/LITRE
DISTILLATION COLUMN        20.0FT HIGH    $150285.50      $0.0015/LITRE
ABSORBER    29.9FT HIGH, 5.31FT DIA       $ 269740.7      $0.0027/LITRE
COMPRESSORS               6495.6 SCFPM    $1664120.0      $0.0169/LITRE
PIPING                       -------      $1195269.0      $0.0121/LITRE
TOTAL EQUIPMENT COST IS $4183442.00   OR  $0.0424/LITRE

NATURAL GAS COST      $   3999.45/DAY   $  0.10082/LITRE
OXYGEN FEED COST      $    801.70/DAY   $  0.02021/LITRE
ELECTRICITY COST      $    457.35/DAY   $  0.01153/LITRE
ENERGY CREDIT:                         $  0.0217/LITRE

METHANOL OUTPUT:  39667.6 LITRES/DAY    TOTAL COST: $0.1533/LITRE
                                        ----------------------
```

Table 53c

```
FOR EXPERIMENT # 26.0

THERMAL  ANALYSIS
-------------------------------

ENERGY INPUTS:
HEAT VALUE OF GAS FEED =   2557263.0 CAL/SEC
COMPRESSOR WORK IN =          4149.9 CAL/SEC
(PUMPING WORK IS NEGLECTED)

USEFUL ENERGY OUTPUT:
EXCESS REACTOR HEAT OF          861006.8 CAL/SEC AT 453.0C
METHANOL HEAT VALUE OF         1270816.0 CAL/SEC
PURGE FLOW HEAT VALUE OF         45277.1 CAL/SEC

LOW GRADE ENERGY OUTPUT:
CO CONVERTER HEAT OF ,          141326.1 CAL/SEC AT 30.0C
OVERHEAD CONDENSOR HEAT OF      153328.7 CAL/SEC AT 64.5C
BOTTOMS WATER FLOW OF               2.26 IGPM AT 105.0C
(  175006.0 CAL/SEC WERE USED TO DRIVE DISTILLATION)
THERMODYNAMIC EFFICIENCY=USEFUL ENERGY OUTPUT / ENERGY INPUT * 100
EFFICIENCY = 2177099.0/2561412.0 *100 =      85.0 %
                                          ---------

COST  ANALYSIS
---------------------------

EQUIPMENT UNIT              SIZE           COST            COST PER LITRE
--------------              ----           ----            --------------
REACTOR                 30525.3 FT**2   $681482.81         $0.0089/LITRE
PREHEATER                5144.9 FT**2   $124867.62         $0.0016/LITRE
DISTILLATION CONDENSOR    351.3 FT**2   $ 12275.02         $0.0002/LITRE
DISTILLATION REBOILER     257.5 FT**2   $ 10996.52         $0.0001/LITRE
CO CONVERTER COOLER       602.5 FT**2   $ 25545.66         $0.0003/LITRE
DISTILLATION COLUMN       23.0FT HIGH   $166625.87         $0.0022/LITRE
ABSORBER    29.9FT HIGH, 5.00FT DIA     $ 268013.9         $0.0035/LITRE
COMPRESSORS              5879.4 SCFPM   $1602272.0         $0.0208/LITRE
PIPING                   --------       $1156831.0         $0.0150/LITRE
TOTAL EQUIPMENT COST IS $4048910.00   OR   $0.0527/LITRE

NATURAL GAS COST      $  3999.45/DAY   $  0.12934/LITRE
OXYGEN FEED COST      $  1056.82/DAY   $  0.03418/LITRE
ELECTRICITY COST      $   416.74/DAY   $  0.01348/LITRE
ENERGY CREDIT:                         $  0.0456/LITRE

METHANOL OUTPUT:  30922.3 LITRES/DAY   TOTAL COST: $0.1841/LITRE
                                       -------------------------
```

```
|---------------------------------------------------------------------
   3     3     3     3     3     3     3     3     3     3
|---------------------------------------------------------------------

FOR EXPERIMENT #26.00
NATURAL GAS FEEDRATE OF  1000000.0 SCF/DAY
MAXIMUM MOLE FRACTION NITROGEN IN REACTANTS OF 0.160
REACTOR PRESSURE OF 734.0 PSIA, TEMPERATURE OF 453.0 DEGREES C
CH4 CONVERSION= 17.400 %   SELECTIVITY= 63.560 %
REACTION BALANCE BASED ON CO2:CO MOLAR RATIO OF      1.503

PROCESS STREAM VALUES ARE TABLED BELOW (ARRAY S(I,J)):
I REFERS TO STREAM NUMBER OF PROCESS FLOWSHEET
P=PSIA, T=DEGREES C, OTHER COLUMNS ARE MOLAR FLOWS (GMOL/SEC)
STEADY STATE ACHIEVED AFTER  63 ITERATIONS:

  I   P   T    CH4     O2      N2      CO     CO2    H2O    CH3OH  TC
|---------------------------------------------------------------------
| 1 734 453 75.320 12.762 17.674  0.0    0.0    0.0     0.0  110.
|---------------------------------------------------------------------
| 2 734 453 62.214  0.0   17.674  1.908  2.868  0.0     0.0  102.
|---------------------------------------------------------------------
| 3 724  42 62.214  0.0   17.674  1.908  2.868  0.0     0.0  102.
|---------------------------------------------------------------------
| 4 718  42 62.214  0.0   17.674  1.908  2.868  0.0     0.0   84.
|---------------------------------------------------------------------
| 5 718  42  0.0    0.0    0.0    0.0    0.0    0.0     0.0   17.
|---------------------------------------------------------------------
| 6  14  64  0.0    0.0    0.0    0.0    0.0    0.0     0.0    8.
|---------------------------------------------------------------------
| 7  16 105  0.0    0.0    0.0    0.0    0.0    0.0     0.0    9.
|---------------------------------------------------------------------
| 8 754  47 62.214  0.0   17.674  1.908  2.868  0.0     0.0   84.
|---------------------------------------------------------------------
| 9 754  47  0.234  0.0    0.066  0.007  0.011  0.0     0.0    0.
|---------------------------------------------------------------------
|10 754  47 61.981  0.0   17.607  1.901  2.857  0.0     0.0   84.
|---------------------------------------------------------------------
|11 752  30 61.981  0.0   17.607  0.0    4.758  0.0     0.0   84.
|---------------------------------------------------------------------
|12 752  30 61.981  0.0   17.607  0.0    0.0    0.0     0.0   84.
|---------------------------------------------------------------------
|13 752  30 61.981  0.0   17.607  0.0    0.0    0.0     0.0   84.
|---------------------------------------------------------------------
|14 734  25 13.336  0.0    0.067  0.0    0.0    0.0     0.0   13.4
|---------------------------------------------------------------------
|15 734  25  0.0   12.762  0.0    0.0    0.0    0.0     0.0   12.7
|---------------------------------------------------------------------
|16 734  25 75.320 12.762 17.674  0.0    0.0    0.0     0.0  110.5
|---------------------------------------------------------------------
```

Table 53d

```
|-----------------------------------------------------------------------|
  18     18     18     18     18     18     18     18     18     18     18
|-----------------------------------------------------------------------|

FOR EXPERIMENT #34.00
NATURAL GAS FEEDRATE OF  1000000.0 SCF/DAY
MAXIMUM MOLE FRACTION NITROGEN IN REACTANTS OF 0.160
REACTOR PRESSURE OF 955.5 PSIA, TEMPERATURE OF 310.0 DEGREES C
CH4 CONVERSION=  7.370 %   SELECTIVITY= 94.570 %
REACTION BALANCE BASED ON CO2:CO MOLAR RATIO OF 99999.875

PROCESS STREAM VALUES ARE TABLED BELOW (ARRAY S(I,J)):
I REFERS TO STREAM NUMBER OF PROCESS FLOWSHEET
P=PSIA, T=DEGREES C, OTHER COLUMNS ARE MOLAR FLOWS (GMOL/SEC)
STEADY STATE ACHIEVED AFTER 140 ITERATIONS:

  I   P   T    CH4      O2     N2      CO      CO2    H2O    CH3OH  TOTAL
|-----------------------------------------------------------------------
|  1 955 310176.865  7.579 35.246  0.0     0.0    0.0     0.0  220.397
|-----------------------------------------------------------------------
|  2 955 310163.830  0.0   35.246  0.000   0.708  0.0     0.0  213.527
|-----------------------------------------------------------------------
|  3 945  38163.830  0.0   35.246  0.000   0.708  0.0     0.0  213.527
|-----------------------------------------------------------------------
|  4 940  38163.830  0.0   35.246  0.000   0.708  0.0     0.0  199.784
|-----------------------------------------------------------------------
|  5 940  38   0.0   0.0    0.0    0.0     0.0    0.0     0.0   13.743
|-----------------------------------------------------------------------
|  6  14  64   0.0   0.0    0.0    0.0     0.0    0.0     0.0   12.430
|-----------------------------------------------------------------------
|  7  16 105   0.0   0.0    0.0    0.0     0.0    0.0     0.0    1.313
|-----------------------------------------------------------------------
|  8 975  41163.830  0.0   35.246  0.000   0.708  0.0     0.0  199.784
|-----------------------------------------------------------------------
|  9 975  41   0.308 0.0    0.066  0.000   0.001  0.0     0.0    0.376
|-----------------------------------------------------------------------
| 10 975  41163.521  0.0   35.180  0.000   0.706  0.0     0.0  199.408
|-----------------------------------------------------------------------
| 11 973  30163.521  0.0   35.180  0.0     0.706  0.0     0.0  199.408
|-----------------------------------------------------------------------
| 12 973  30163.521  0.0   35.180  0.0     0.0    0.0     0.0  199.408
|-----------------------------------------------------------------------
| 13 973  30163.521  0.0   35.180  0.0     0.0    0.0     0.0  199.408
|-----------------------------------------------------------------------
| 14 955  25 13.336  0.0    0.067  0.0     0.0    0.0     0.0   13.403
|-----------------------------------------------------------------------
| 15 955  25  0.0    7.579  0.0    0.0     0.0    0.0     0.0    7.579
|-----------------------------------------------------------------------
| 16 955  25176.865  7.579 35.246  0.0     0.0    0.0     0.0  220.397
|-----------------------------------------------------------------------
```

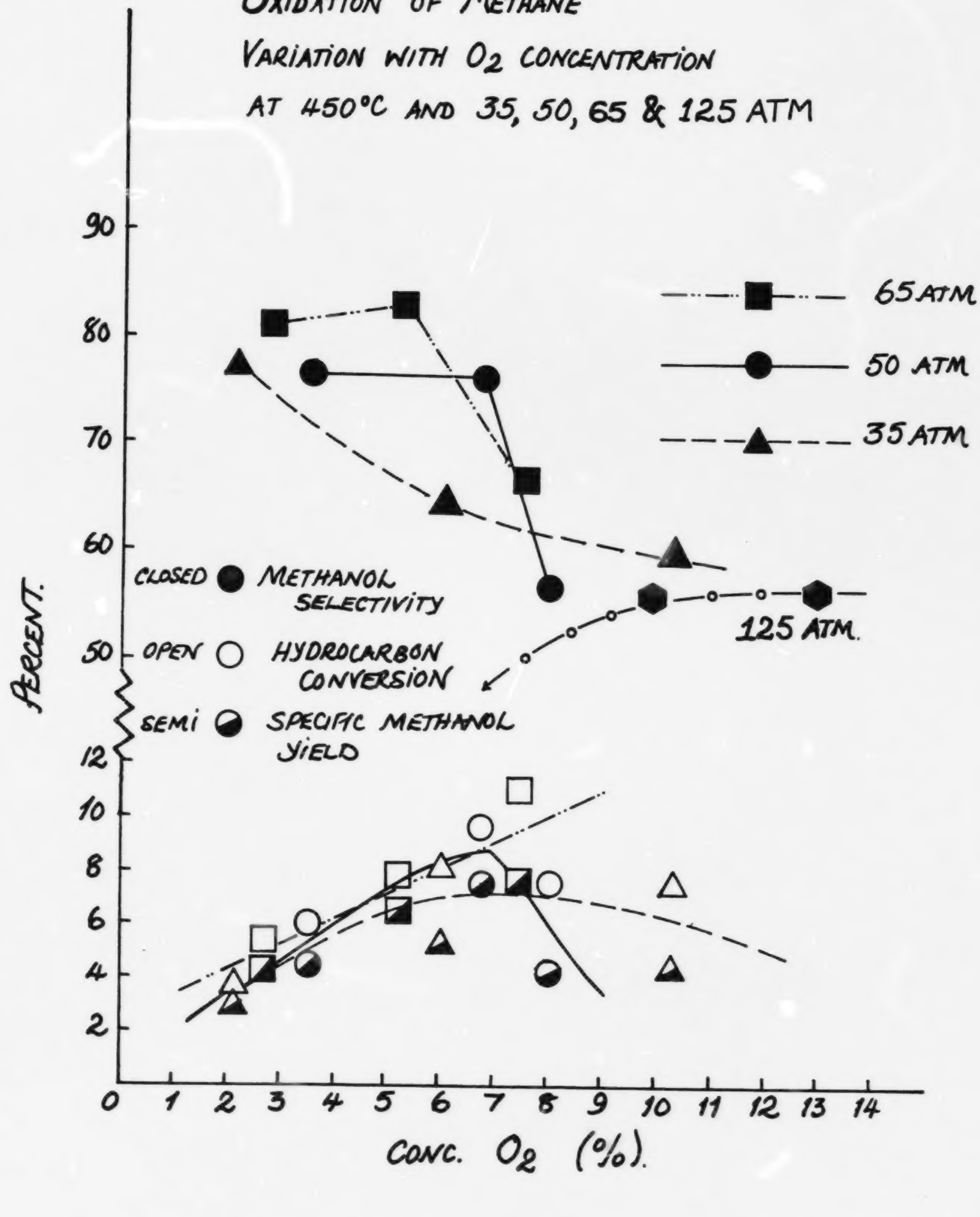
```
FOR EXPERIMENT # 34.0

T H E R M A L   A N A L Y S I S
-------------------------------

E N E R G Y   I N P U T S :
HEAT VALUE OF GAS FEED =    2557263.0 CAL/SEC
COMPRESSOR WORK IN =           7451.6 CAL/SEC
(PUMPING WORK IS NEGLECTED)

U S E F U L   E N E R G Y   O U T P U T :
EXCESS REACTOR HEAT OF           -220878.4 CAL/SEC AT 310.0C
METHANOL HEAT VALUE OF           1881208.0 CAL/SEC
PURGE FLOW HEAT VALUE OF           59155.9 CAL/SEC

L O W   G R A D E   E N E R G Y   O U T P U T :
CO CONVERTER HEAT OF ,             20834.8 CAL/SEC AT 30.0C
OVERHEAD CONDENSOR HEAT OF        719891.9 CAL/SEC AT 64.5C
BOTTOMS WATER FLOW OF                 0.31 IGPM AT 105.0C
(   729944.2 CAL/SEC WERE USED TO DRIVE DISTILLATION)
THERMODYNAMIC EFFICIENCY=USEFUL ENERGY OUTPUT / ENERGY INPUT * 10
EFFICIENCY = 1719484.0/2564714.0 *100 =     67.0 %
                                         ---------

C O S T   A N A L Y S I S
-------------------------

EQUIPMENT UNIT               SIZE          COST          COST PER LITR
--------------.              ----          ----          -------------
REACTOR                  82183.1 FT**2  $*********       $0.0183/LITR
PREHEATER                 7729.0 FT**2  $207801.94       $0.0018/LITR
DISTILLATION CONDENSOR 1649.2 FT**2  $ 29975.67       $0.0003/LITR
DISTILLATION REBOILER  1074.0 FT**2  $ 22132.43       $0.0002/LITR
CO CONVERTER COOLER     167.7 FT**2  $ 18170.94       $0.0002/LITR
DISTILLATION COLUMN     14.0FT HIGH  $117604.69       $0.0010/LITR
ABSORBER     29.9FT HIGH, 7.78FT DIA  $ 294405.0       $0.0026/LITR
COMPRESSORS              13873.9 SCFPM  $2220368.0       $0.0195/LITR
PIPING                      -------     $1994922.0       $0.0175/LITR
TOTAL EQUIPMENT COST IS $6982228.00  OR  $0.0614/LITRE

NATURAL GAS COST      $  3999.45/DAY  $  0.08737/LITRE
OXYGEN FEED COST      $   627.61/DAY  $  0.01371/LITRE
ELECTRICITY COST      $   748.29/DAY  $  0.01635/LITRE
ENERGY CREDIT:                       $  -0.0055/LITRE

METHANOL OUTPUT:  45774.8 LITRES/DAY   TOTAL COST: $0.1843/LITRE
                                       -------------------------
```

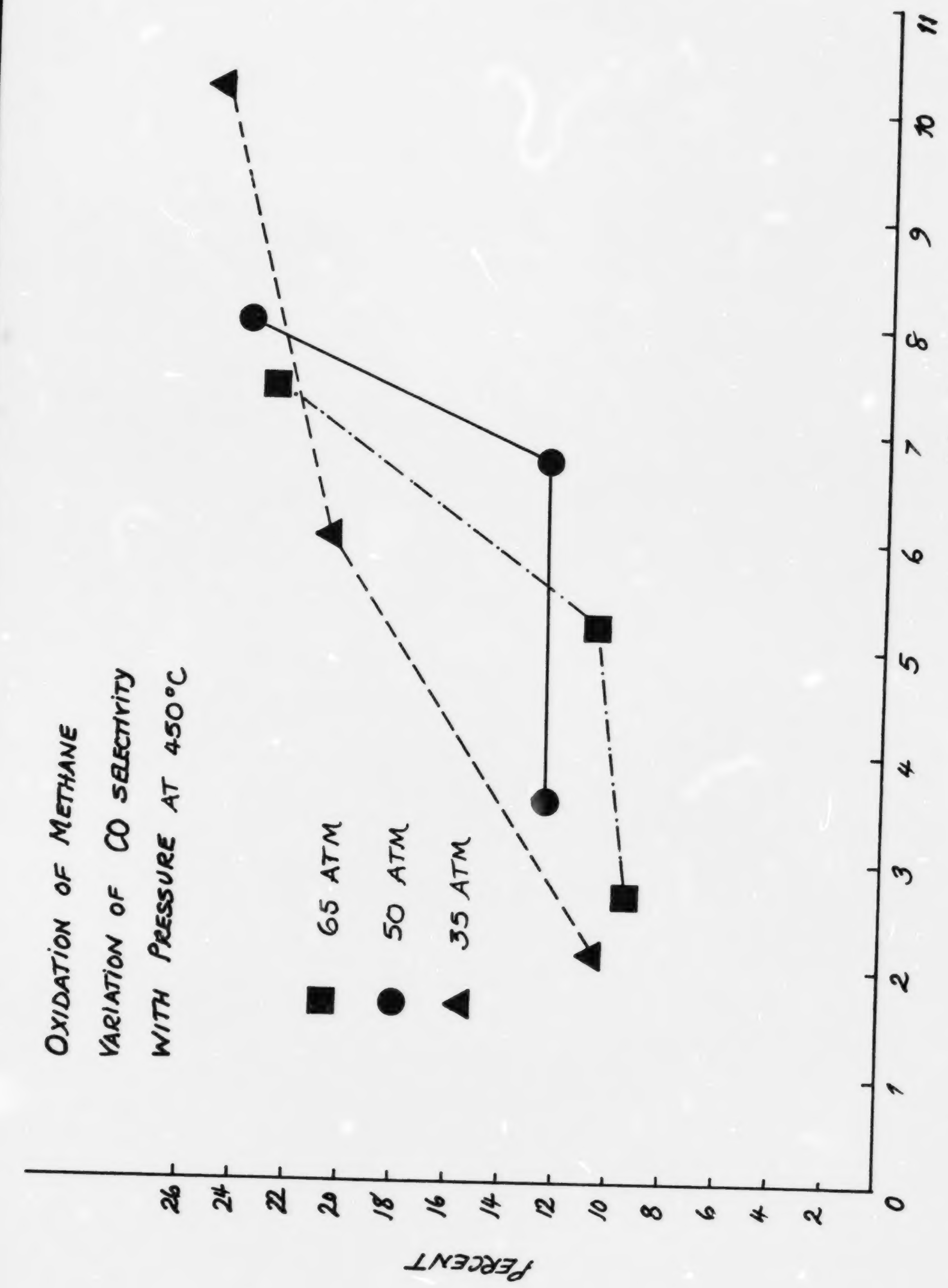
Table 53e

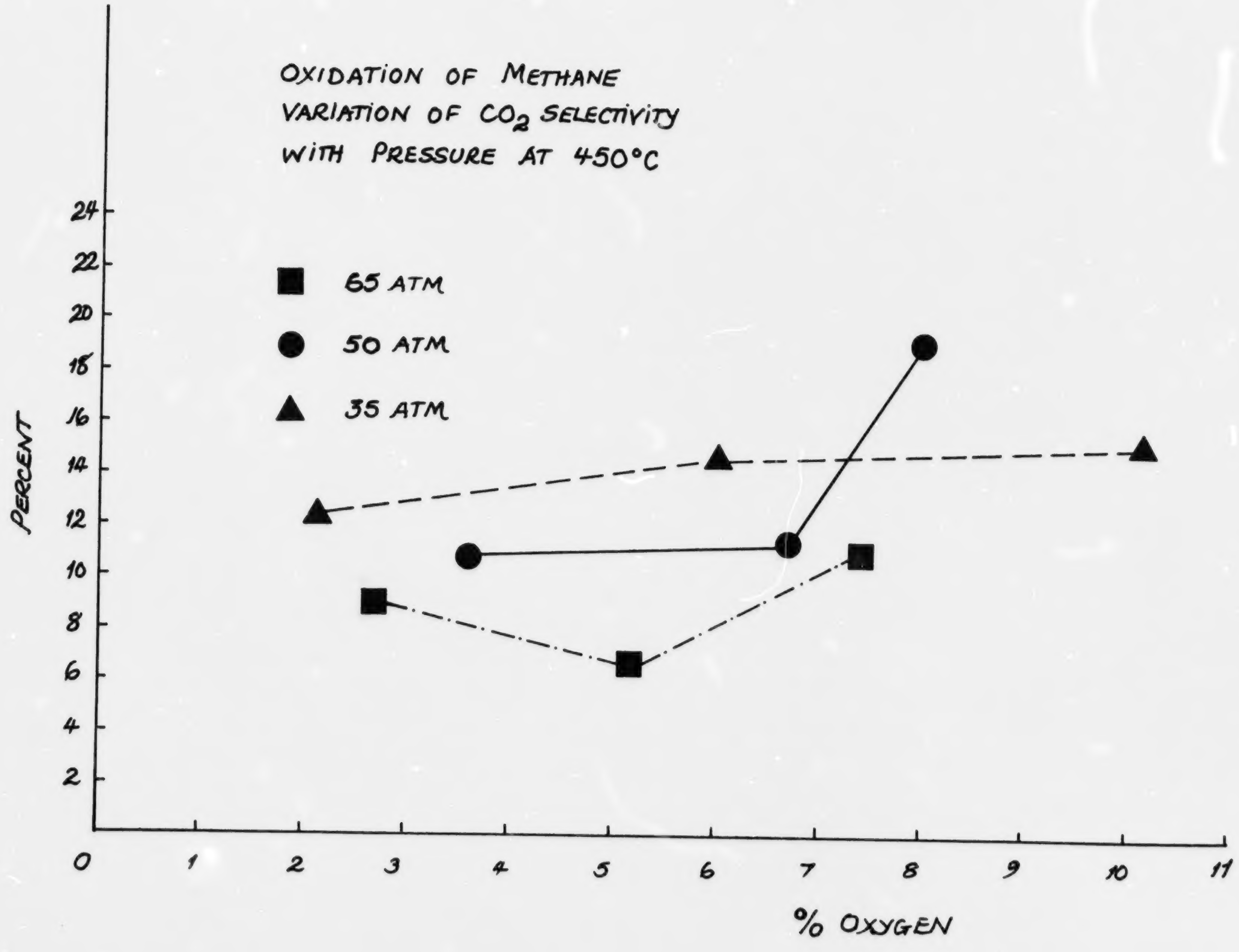
```
|---------------------------------------------------------------------------|
   24    24    24    24    24    24    24    24    24    24    24
|---------------------------------------------------------------------------|

FOR EXPERIMENT #38.00
NATURAL GAS FEEDRATE OF  1000000.0 SCF/DAY
MAXIMUM MOLE FRACTION NITROGEN IN REACTANTS OF 0.160
REACTOR PRESSURE OF 514.5 PSIA, TEMPERATURE OF 350.0 DEGREES C
CH4 CONVERSION=  8.390 %   SELECTIVITY= 87.490 %
REACTION BALANCE BASED ON CO2:CO MOLAR RATIO OF      3.568

PROCESS STREAM VALUES ARE TABLED BELOW (ARRAY S(I,J)):
I REFERS TO STREAM NUMBER OF PROCESS FLOWSHEET
P=PSIA, T=DEGREES C, OTHER COLUMNS ARE MOLAR FLOWS (GMOL/SEC)
STEADY STATE ACHIEVED AFTER 125 ITERATIONS:

  I   P  T     CH4      O2     N2     CO      CO2    H2O    CH3OH  TOTAL
 --------------------------------------------------------------------------
  1 514 350155.466  8.791 31.579  0.0    0.0    0.0     0.0  197.465
 --------------------------------------------------------------------------
  2 514 350142.423  0.0   31.579  0.357  1.275  0.0     0.0  190.309
 --------------------------------------------------------------------------
  3 504  39142.423  0.0   31.579  0.357  1.275  0.0     0.0  190.309
 --------------------------------------------------------------------------
  4 499  39142.423  0.0   31.579  0.357  1.275  0.0     0.0  175.634
 --------------------------------------------------------------------------
  5 499  39  0.0    0.0    0.0    0.0    0.0    0.0     0.0   14.675
 --------------------------------------------------------------------------
  6  14  64  0.0    0.0    0.0    0.0    0.0    0.0     0.0   11.507
 --------------------------------------------------------------------------
  7  16 105  0.0    0.0    0.0    0.0    0.0    0.0     0.0    3.169
 --------------------------------------------------------------------------
  8 534  45142.423  0.0   31.579  0.357  1.275  0.0     0.0  175.634
 --------------------------------------------------------------------------
  9 534  45  0.299  0.0    0.066  0.001  0.003  0.0     0.0    0.369
 --------------------------------------------------------------------------
 10 534  45142.123  0.0   31.513  0.356  1.272  0.0     0.0  175.265
 --------------------------------------------------------------------------
 11 532  30142.123  0.0   31.513  0.0    1.628  0.0     0.0  175.265
 --------------------------------------------------------------------------
 12 532  30142.123  0.0   31.513  0.0    0.0    0.0     0.0  175.265
 --------------------------------------------------------------------------
 13 532  30142.123  0.0   31.513  0.0    0.0    0.0     0.0  175.265
 --------------------------------------------------------------------------
 14 514  25 13.336  0.0    0.067  0.0    0.0    0.0     0.0   13.403
 --------------------------------------------------------------------------
 15 514  25  0.0    8.791  0.0    0.0    0.0    0.0     0.0    8.791
 --------------------------------------------------------------------------
 16 514  25155.466  8.791 31.579  0.0    0.0    0.0     0.0  197.465
 --------------------------------------------------------------------------
```

```
FOR EXPERIMENT # 38.0

T H E R M A L   A N A L Y S I S
-------------------------------

E N E R G Y   I N P U T S :
HEAT VALUE OF GAS FEED =    2557263.0 CAL/SEC
COMPRESSOR WORK IN =          12060.6 CAL/SEC
(PUMPING WORK IS NEGLECTED)

U S E F U L   E N E R G Y   O U T P U T :
EXCESS REACTOR HEAT OF             380818.4 CAL/SEC AT 350.0C
METHANOL HEAT VALUE OF            1741443.0 CAL/SEC
PURGE FLOW HEAT VALUE OF            57456.9 CAL/SEC

L O W   G R A D E   E N E R G Y   O U T P U T :
CO CONVERTER HEAT OF ,              48196.9 CAL/SEC AT 30.0C
OVERHEAD CONDENSOR HEAT OF         239114.9 CAL/SEC AT 64.5C
BOTTOMS WATER FLOW OF                  0.75 IGPM AT 105.0C
(  252927.4 CAL/SEC WERE USED TO DRIVE DISTILLATION)
THERMODYNAMIC EFFICIENCY=USEFUL ENERGY OUTPUT / ENERGY INPUT * 10
EFFICIENCY = 2179717.0/2569323.0 *100 =      84.8 %
                                            ---------

C O S T   A N A L Y S I S
-------------------------

EQUIPMENT UNIT                 SIZE           COST              COST PER LITR
--------------                 ----           ----              -------------
REACTOR                     65450.8 FT**2  $*********          $0.0118/LITR
PREHEATER                    7813.0 FT**2  $157094.12          $0.0015/LITR
DISTILLATION CONDENSOR        547.8 FT**2  $ 14955.17          $0.0001/LITR
DISTILLATION REBOILER         372.2 FT**2  $ 12560.16          $0.0001/LITR
CO CONVERTER COOLER           272.9 FT**2  $ 15648.53          $0.0001/LITR
DISTILLATION COLUMN           17.0FT HIGH  $133945.06          $0.0013/LITR
ABSORBER      29.9FT HIGH, 7.29FT DIA      $ 273537.9          $0.0026/LITR
COMPRESSORS                12196.8 SCFPM   $2114284.0          $0.0201/LITR
PIPING                        -------      $1584781.0          $0.0150/LITR
TOTAL EQUIPMENT COST IS $5546736.00     OR   $0.0527/LITRE

NATURAL GAS COST        $  3999.45/DAY  $  0.09438/LITRE
OXYGEN FEED COST        $   727.95/DAY  $  0.01718/LITRE
ELECTRICITY COST        $  1211.13/DAY  $  0.02858/LITRE
ENERGY CREDIT:                        $  0.0161/LITRE

METHANOL OUTPUT:  42373.9 LITRES/DAY     TOTAL COST: $0.1767/LITRE
                                         -------------------------

END OF DATA AFTER 24 SIMULATIONS.

|------------------------------------------------------------------------
```

OXIDATION OF METHANE
VARIATION WITH O_2 CONCENTRATION
AT 450°C AND 35, 50, 65 & 125 ATM

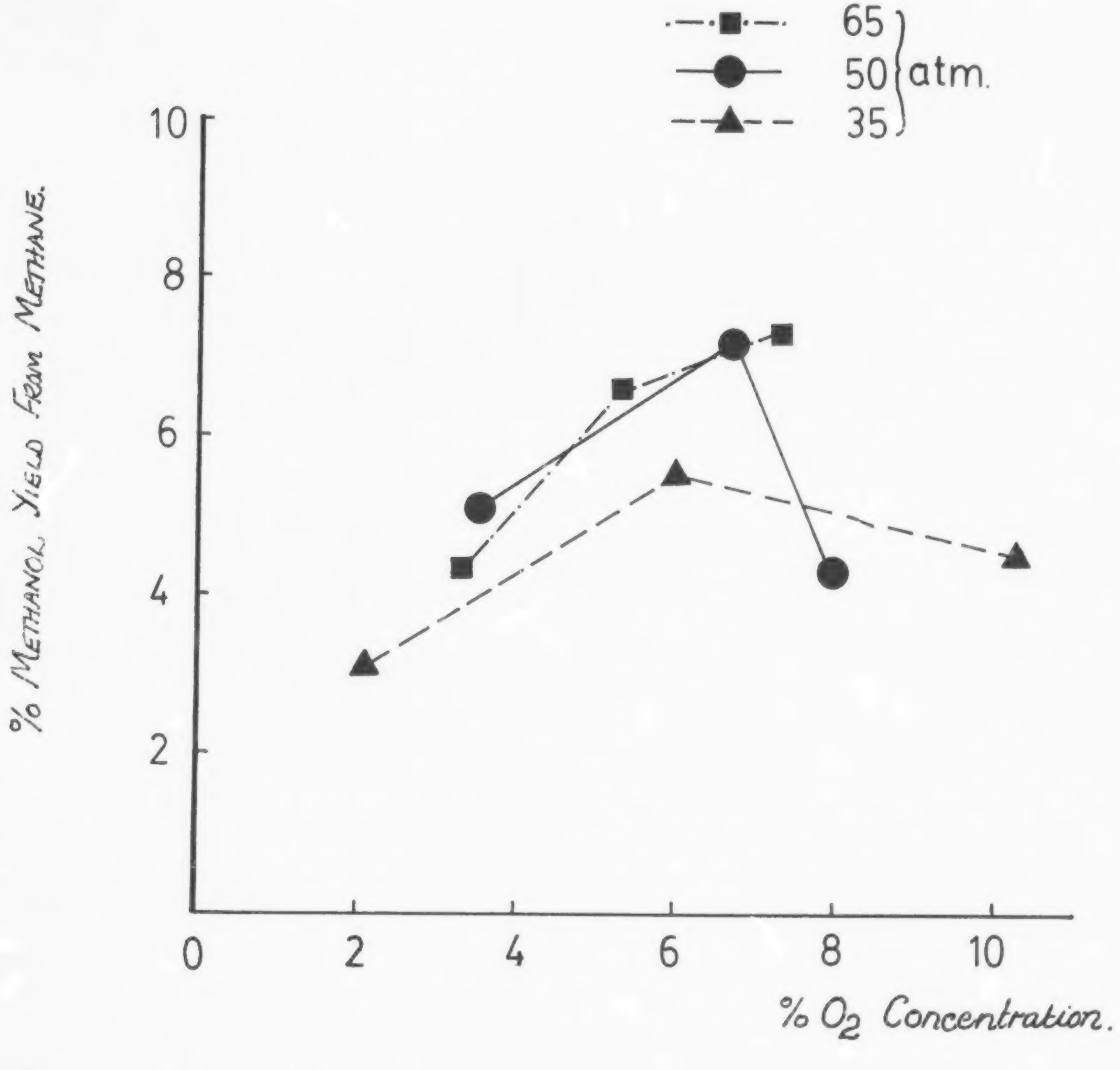


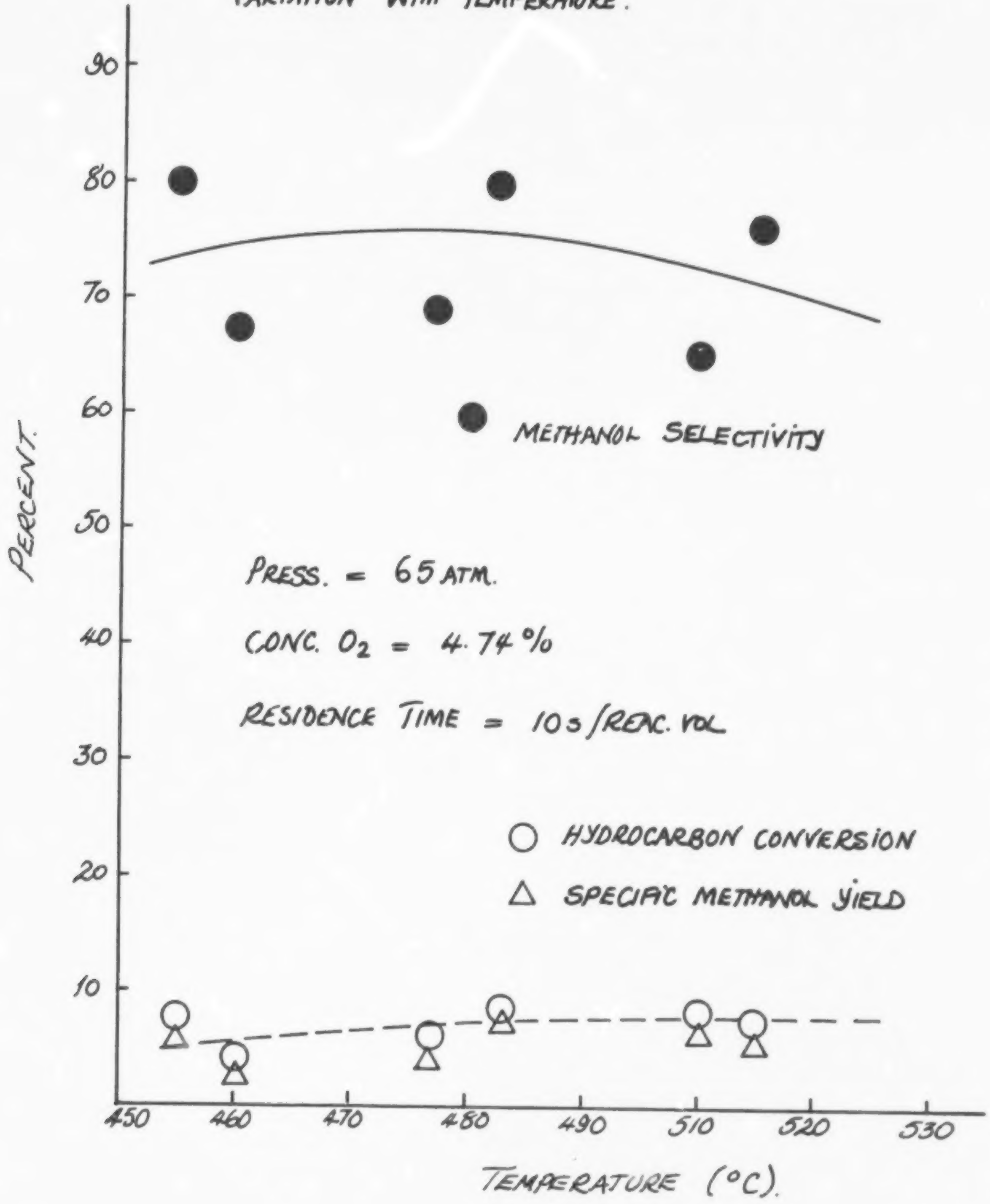

OXIDATION OF METHANE
VARIATION OF CO SELECTIVITY
WITH PRESSURE AT 450°C
■ 65 ATM
● 50 ATM
▲ 35 ATM
PERCENT
26
24
22
20
18
16
14
12
10
8
6
4
2
0
1
2
3
4
5
6
7
8
9
10
11
% OXYGEN



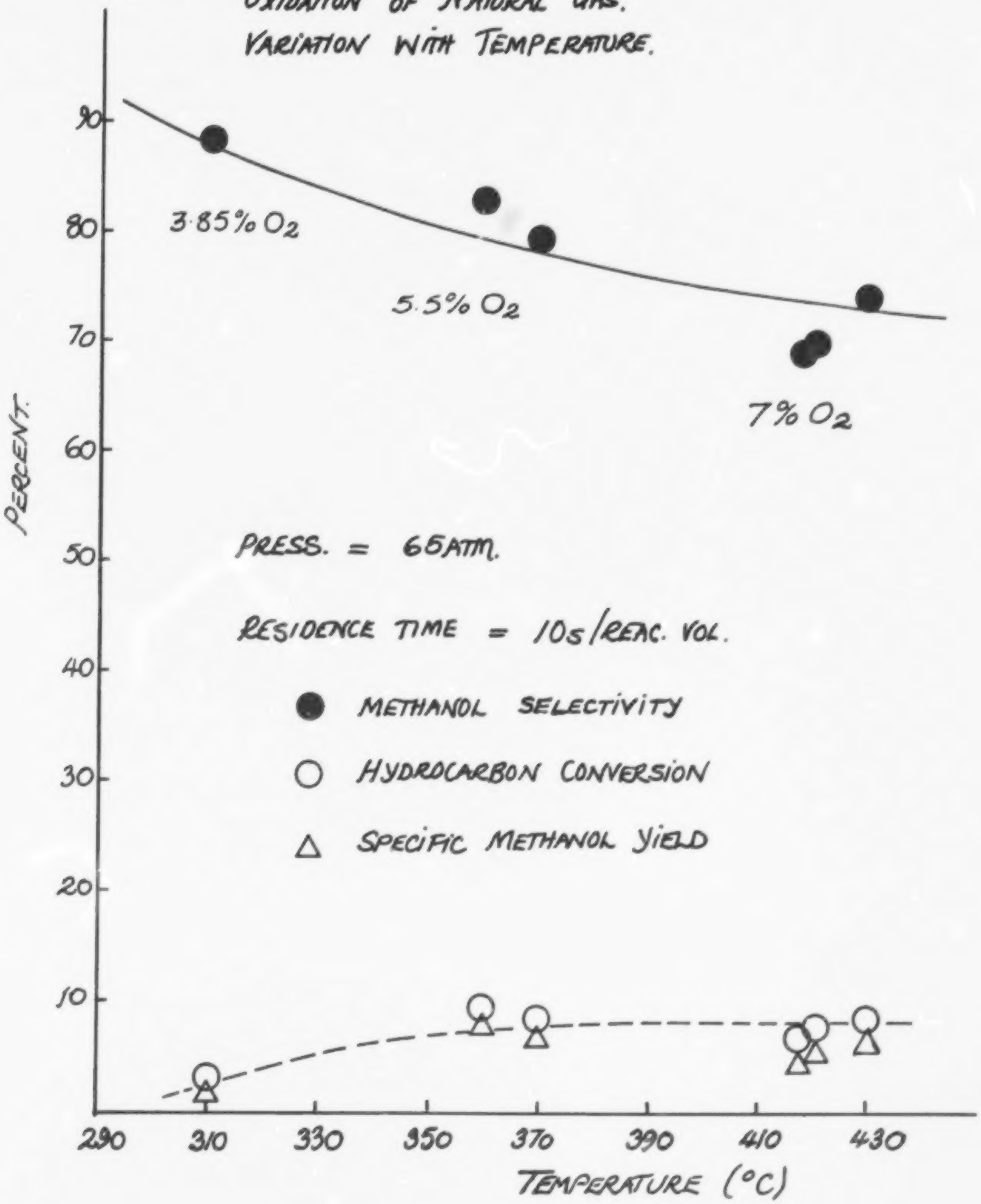
OXIDATION OF METHANE
VARIATION OF CO_2 SELECTIVITY
WITH PRESSURE AT 450°C

FIGURE 4. VARIATION OF METHANOL YIELD AS A FUNCTION OF O_2 CONCENTRATION WITH PRESSURE.

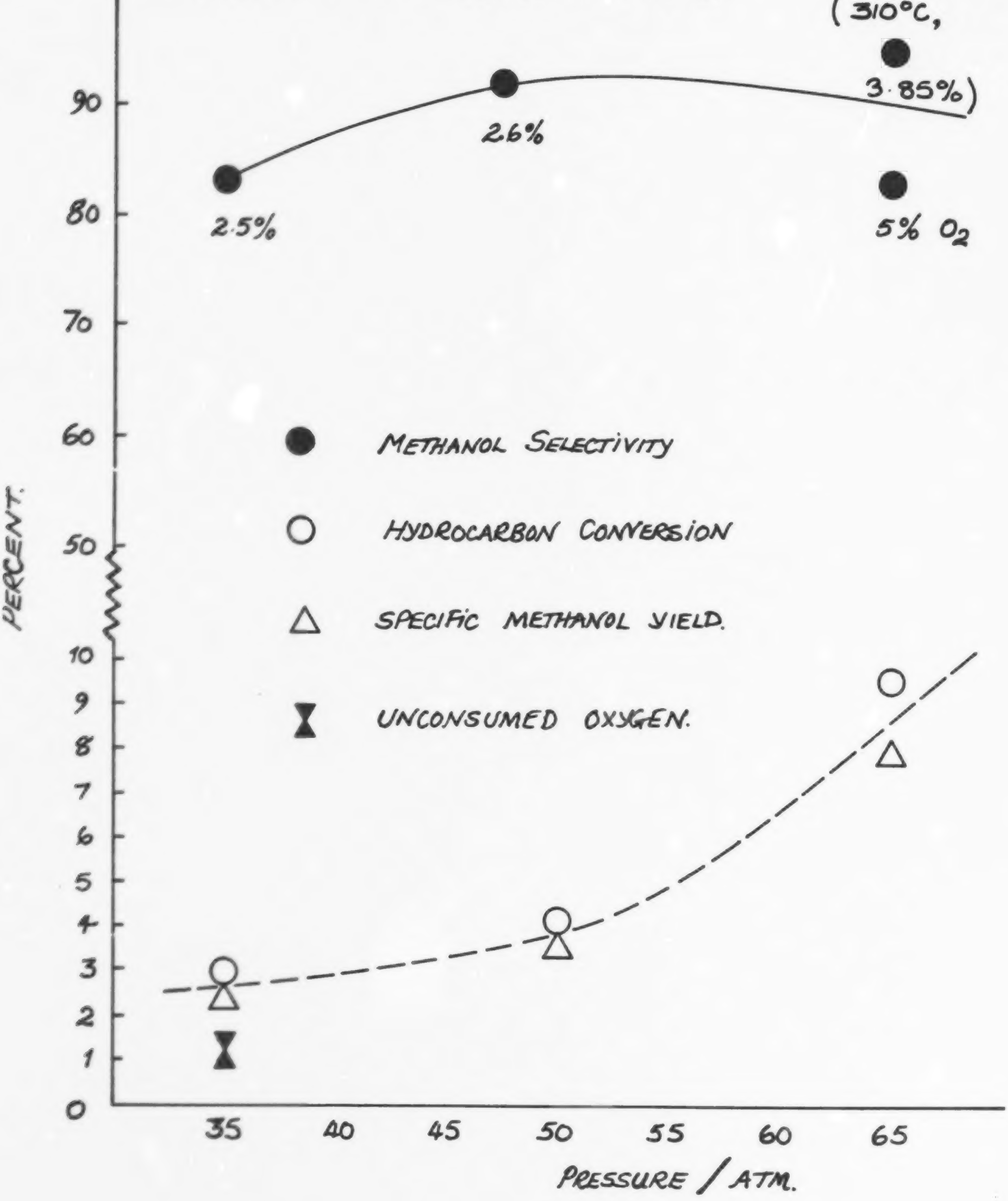


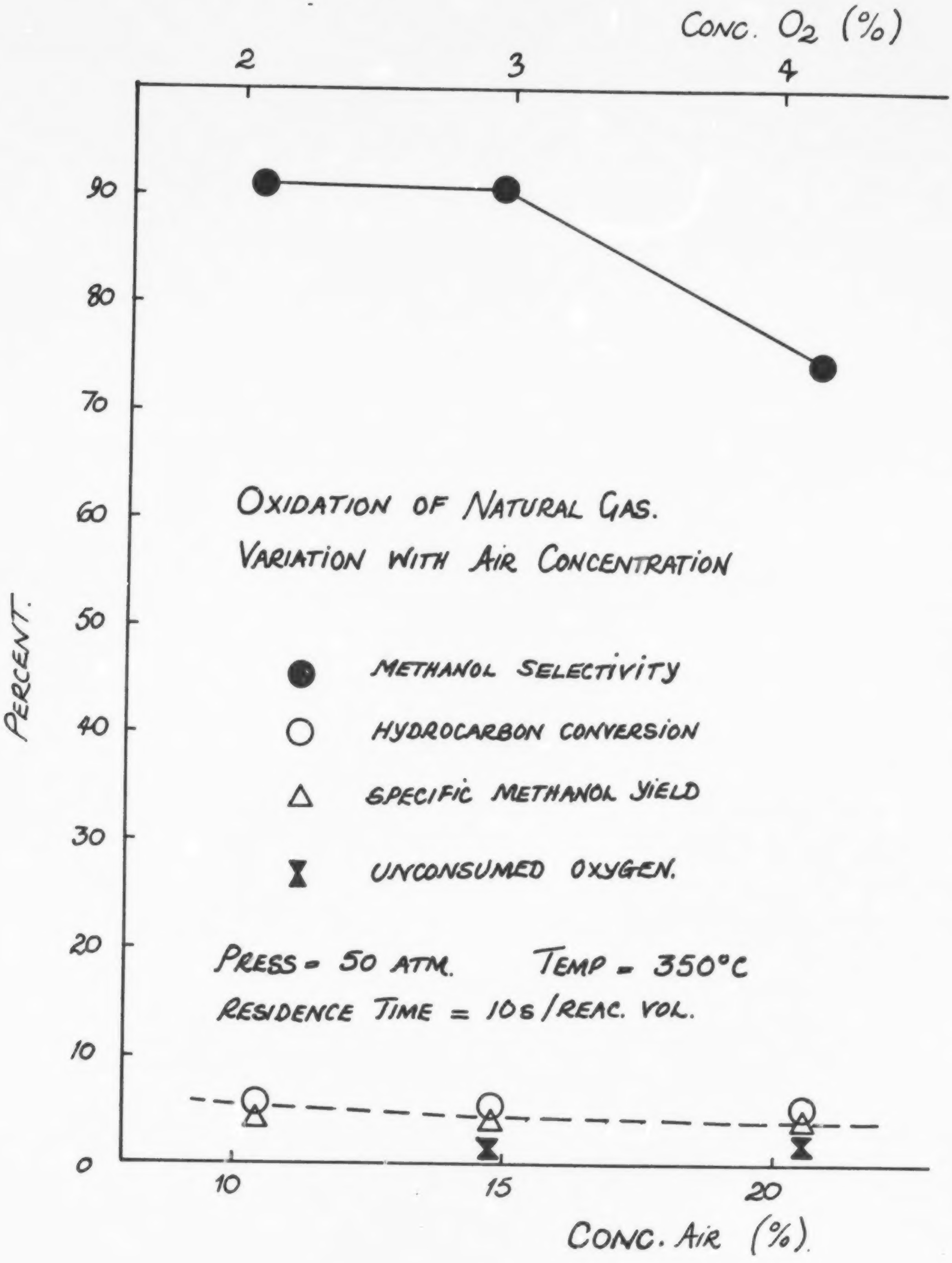


OXIDATION OF METHANE
VARIATION WITH TEMPERATURE.


OXIDATION OF NATURAL GAS.
VARIATION WITH TEMPERATURE.
PERCENT.
90
80
70
60
50
40
30
20
10
3·85% O_2
5.5% O_2
7% O_2
PRESS. = 65ATM.
RESIDENCE TIME = 10s/REAC. VOL.
● METHANOL SELECTIVITY
○ HYDROCARBON CONVERSION
△ SPECIFIC METHANOL YIELD
290
310
330
350
370
390
410
430
TEMPERATURE (°C)

OXIDATION OF NATURAL GAS
VARIATION WITH PRESSURE AT 350°C.




CONC. O_2 (%)
2
3
4
90
80
70
60
50
40
30
20
10
0
PERCENT.
OXIDATION OF NATURAL GAS.
VARIATION WITH AIR CONCENTRATION
● METHANOL SELECTIVITY
○ HYDROCARBON CONVERSION
△ SPECIFIC METHANOL YIELD
⧗ UNCONSUMED OXYGEN.
PRESS = 50 ATM. TEMP = 350°C
RESIDENCE TIME = 10s/REAC. VOL.
10
15
20
CONC. AIR (%)

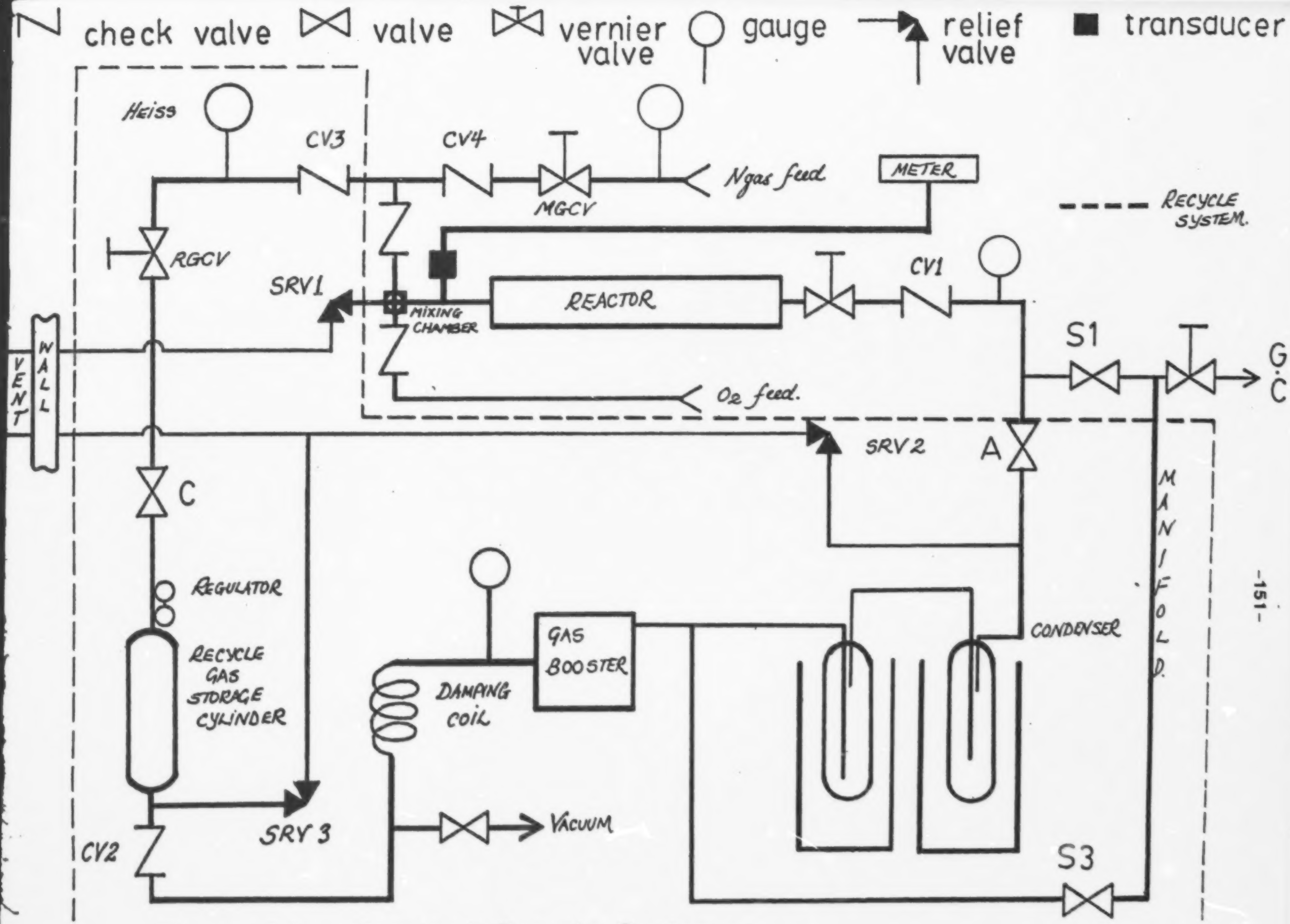

check valve
valve
vernier valve
gauge
relief valve
transducer
RECYCLE SYSTEM.
Heiss
CV3
CV4
MGCV
Ngas feed
METER
RGCV
SRV1
MIXING CHAMBER
REACTOR
CV1
S1
G·C
O2 feed.
VENT
WALL
SRV 2
A
C
MANIFOLD.
REGULATOR
RECYCLE GAS STORAGE CYLINDER
GAS BOOSTER
CONDENSER
DAMPING COIL
SRY 3
CV2
VACUUM
S3

Figure 5.1 Reactor & Recycle Systems.

10 X 10 TO THE CM

FIGURE 10. VARIATION OF CH_3OH YIELD AND NGAS CONVERSION WITH FLOW RATE (NTP) AT 10 ATM & 4·2% O_2.

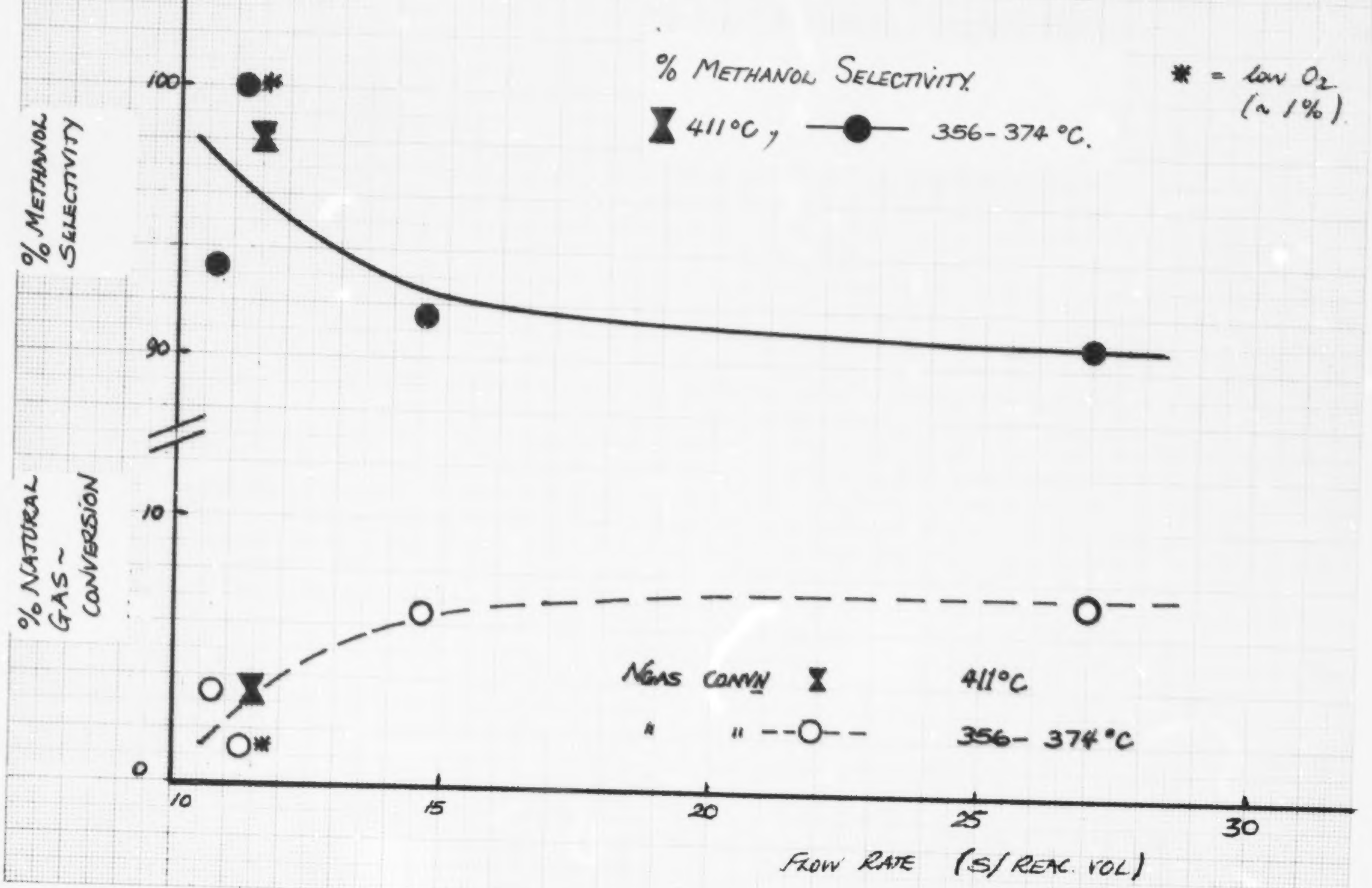


FIGURE 11. VARIATION OF CH_3OH SELECTIVITY & NGAS CONVERSION WITH TEMP. AT ATMOSPHERIC PRESSURE AND 10% O_2

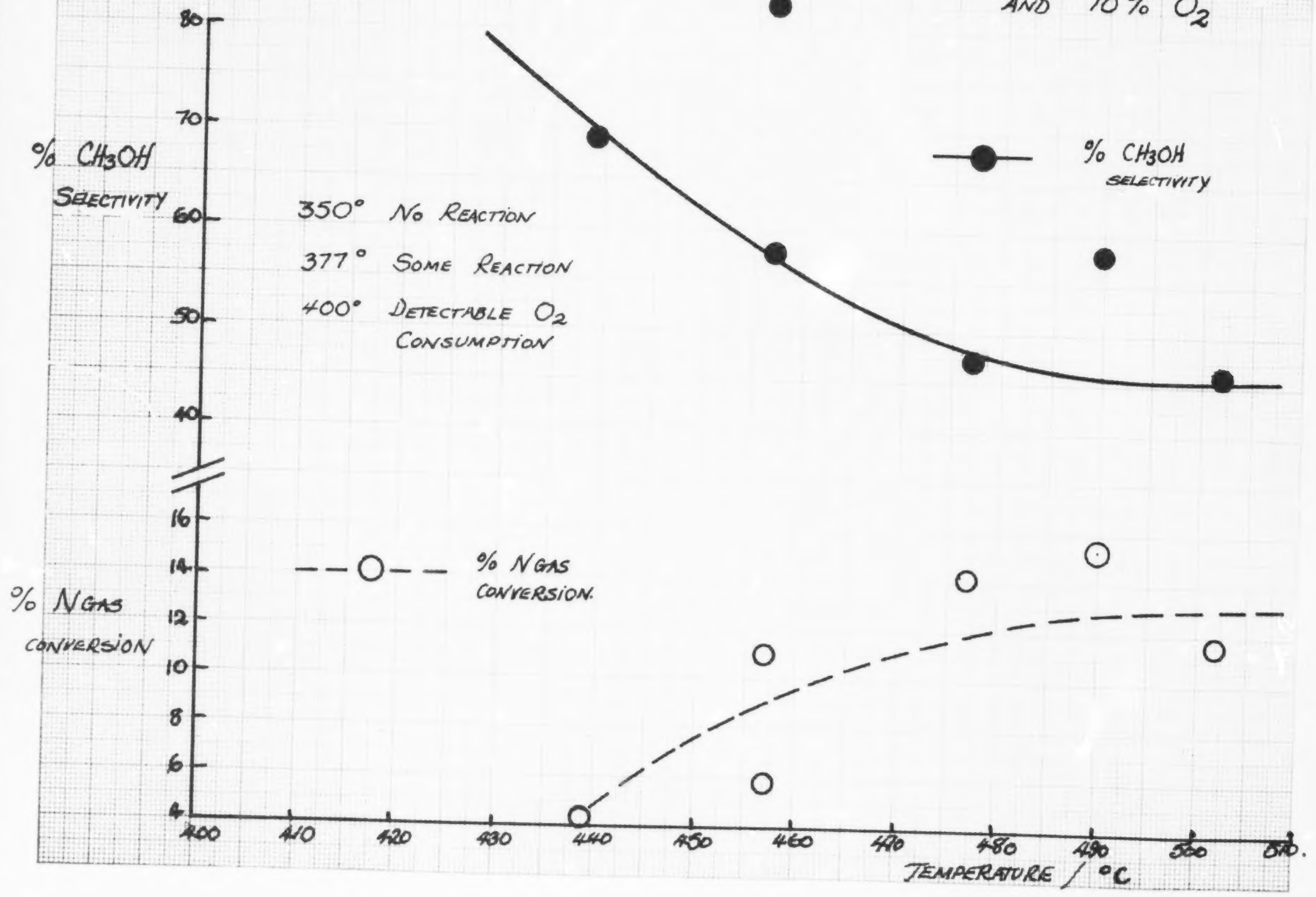
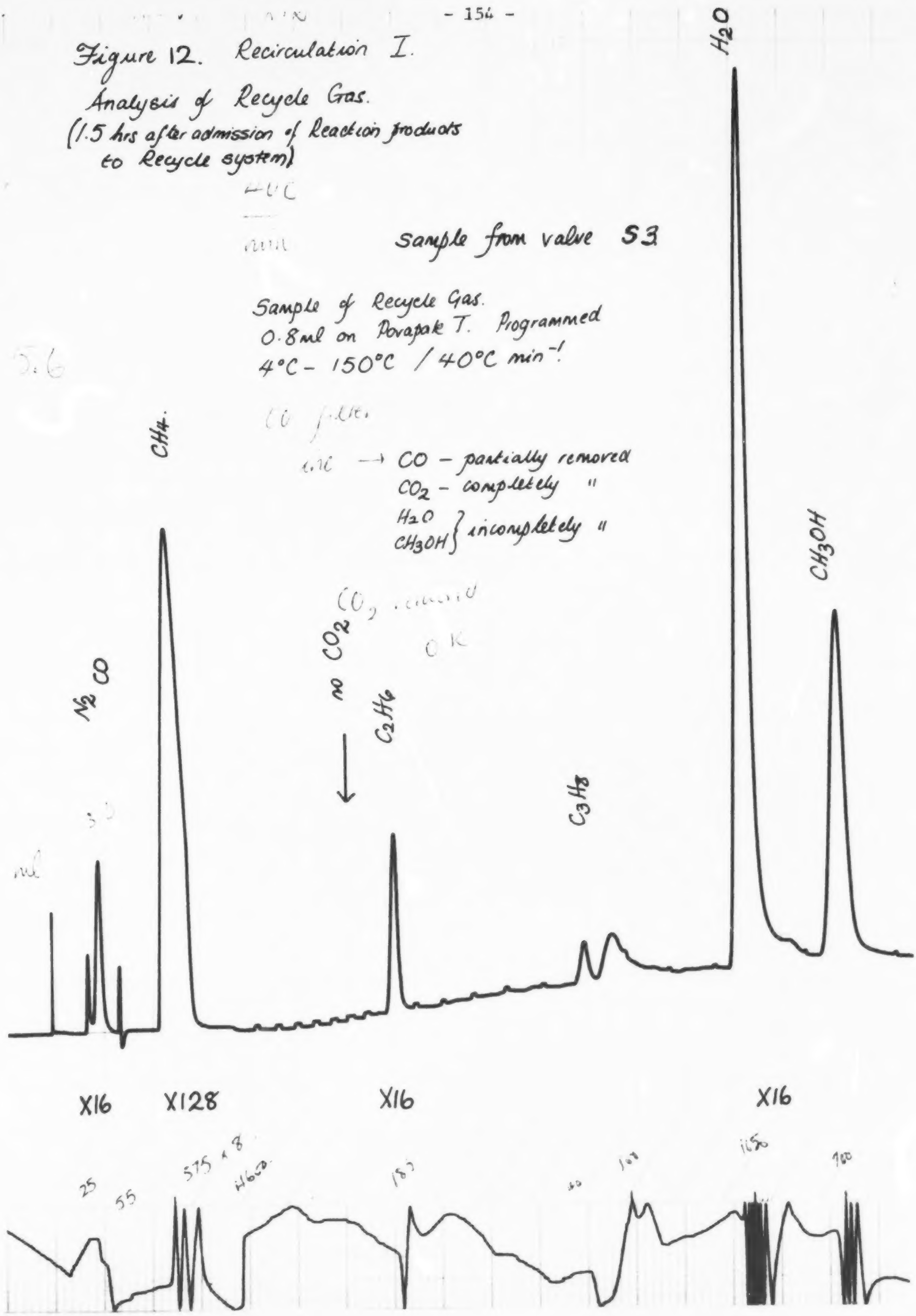


Figure 12. Recirculation I.

Analysis of Recycle Gas.
(1.5 hrs after admission of Reaction products to Recycle system)



sample from valve S3

Sample of Recycle Gas.
0.8ml on Porapak T. Programmed
4°C - 150°C / 40°C min^{-1}.

→ CO - partially removed
CO_2 - completely "
H_2O
CH_3OH } incompletely "

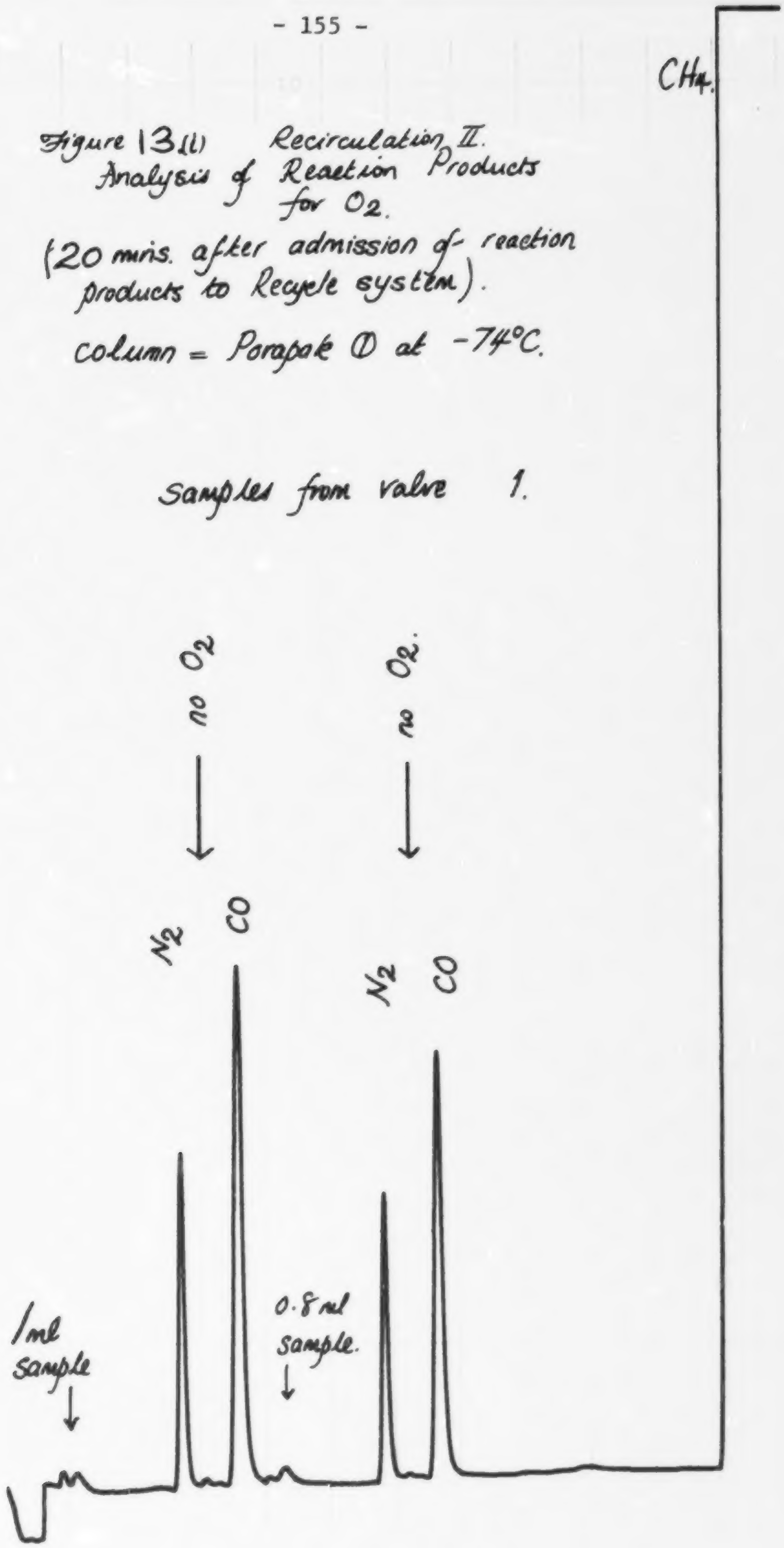


Figure 13(i) Recirculation II.
Analysis of Reaction Products for O_2.
(20 mins. after admission of reaction products to Recycle system).
column = Porapak Q at -74°C.

samples from valve 1.

Figure 13 (ii) Recirculation II.
Analysis of Recycle Gas.
for CO and CO_2
(2 hrs 50 mins after admission of Reaction products to Recycle system).

Column = Porapak T. 4°C - 150°C @ 40°C/min

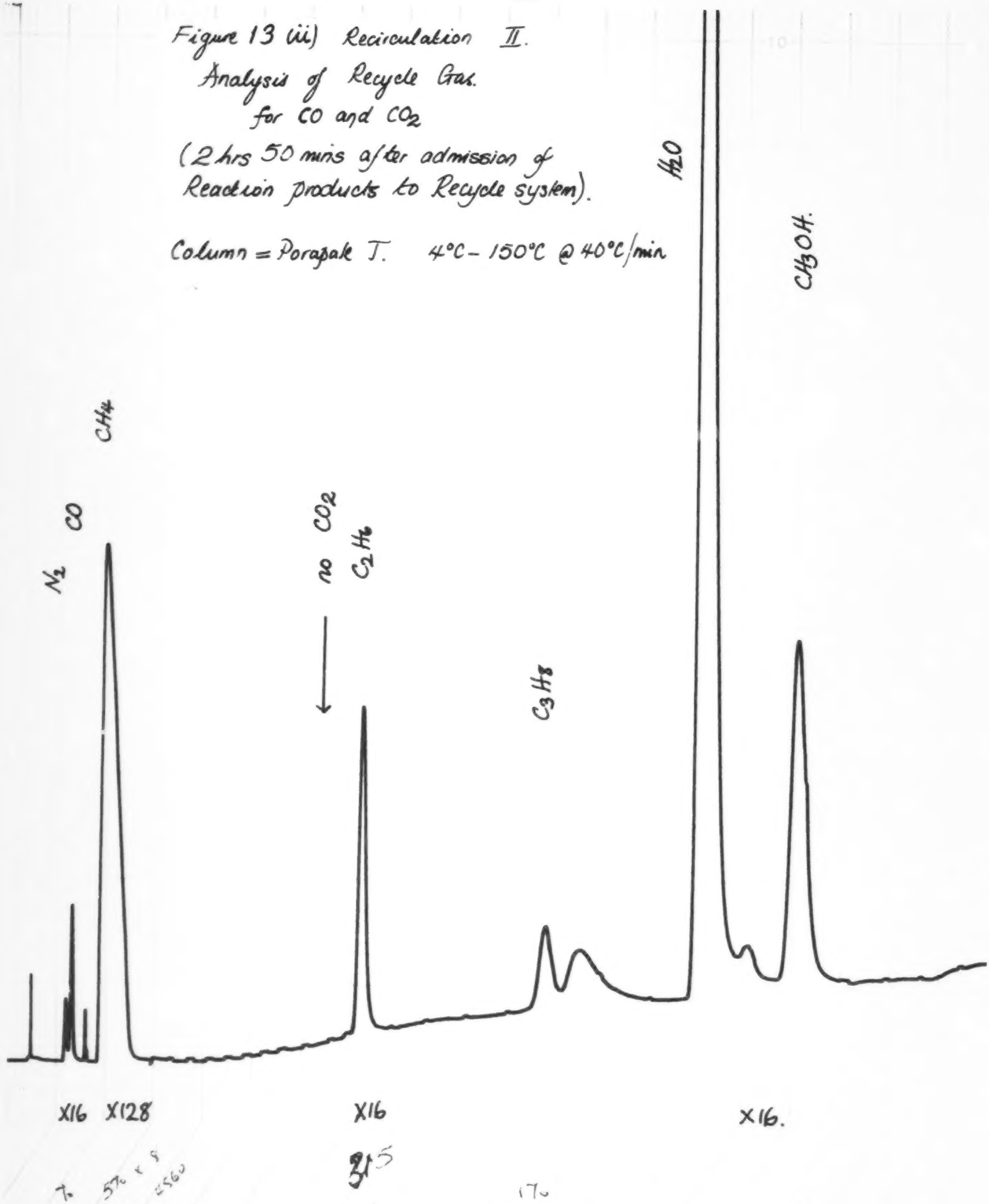
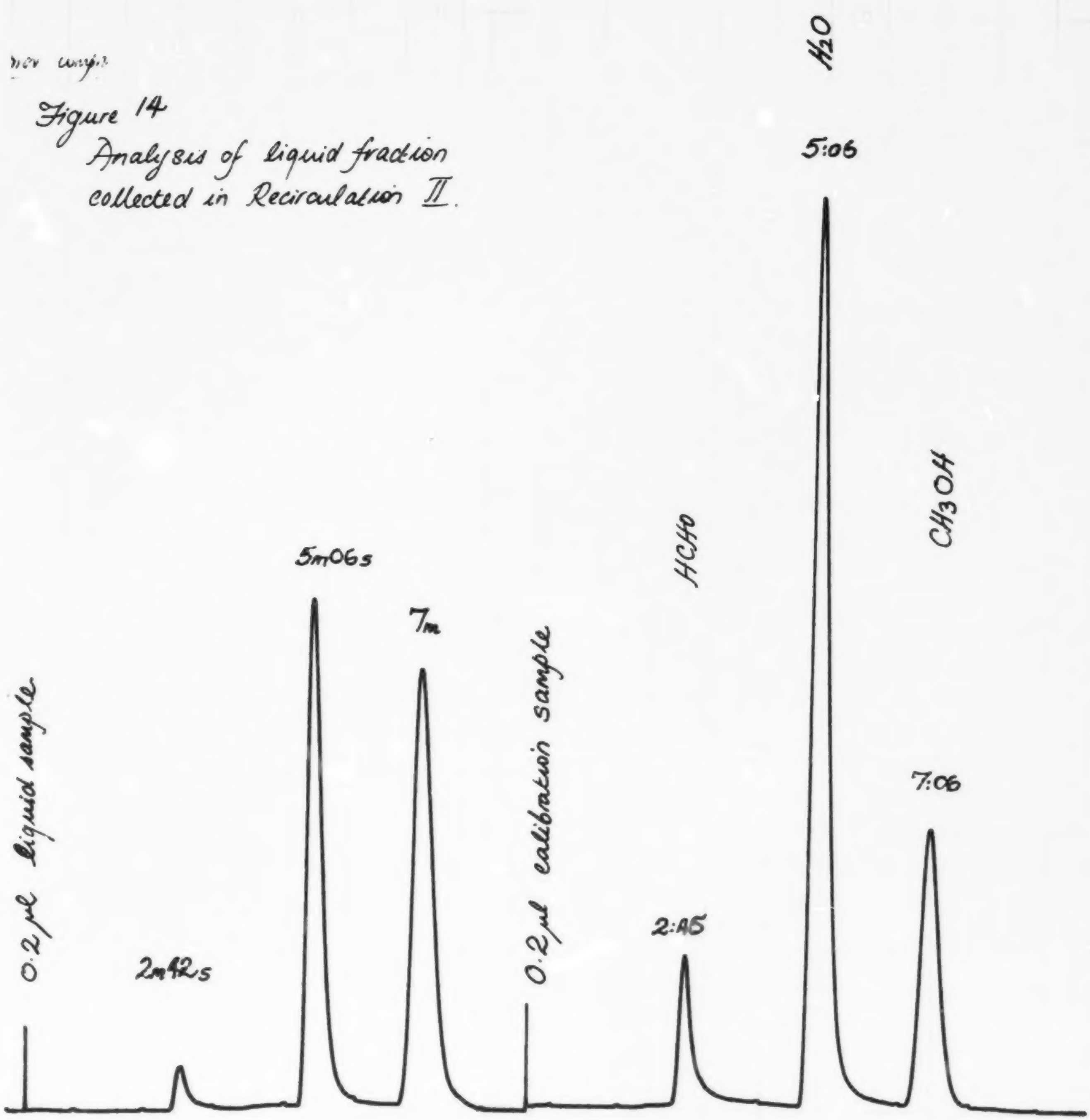


Figure 14
Analysis of liquid fraction collected in Recirculation II.



Column = Porapak T.
col. temp = 150°C isothermal.
col. flow = 25ml/min He.

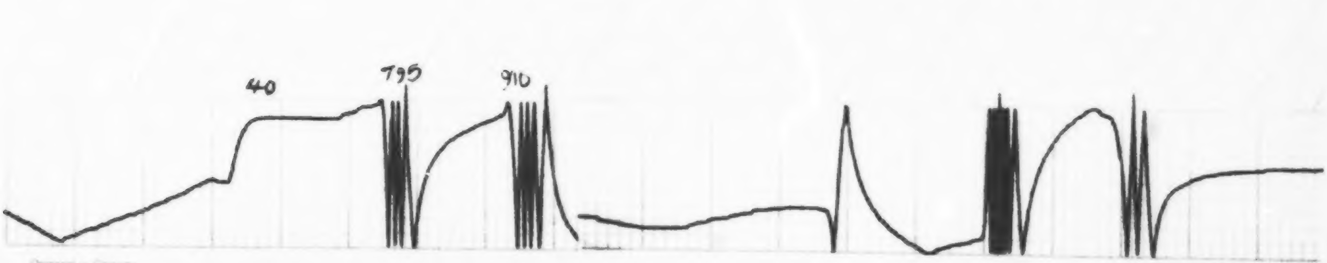


Figure 15 ω Recirculation III
Analysis of reaction products.
(prior to recirculation).

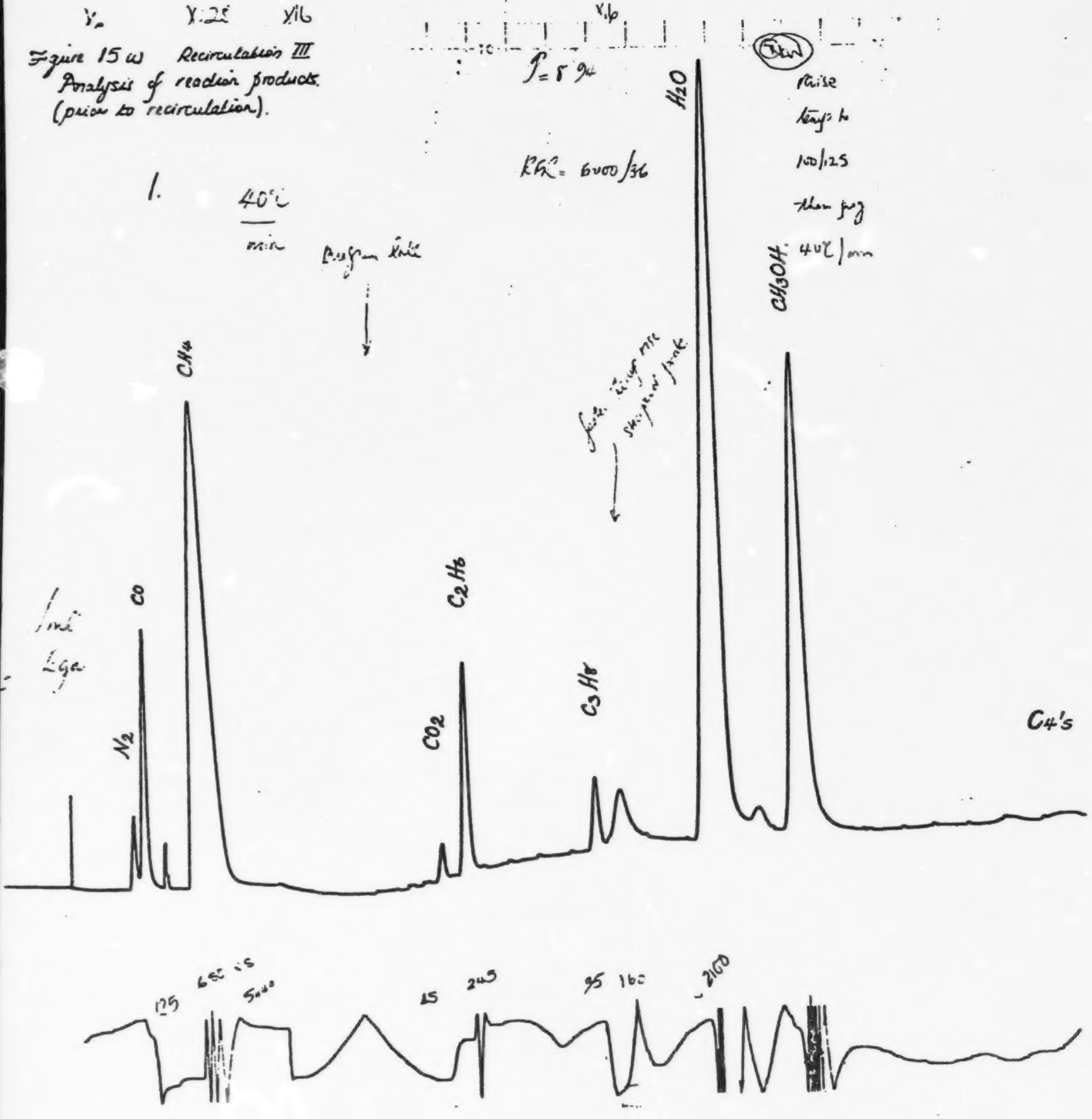
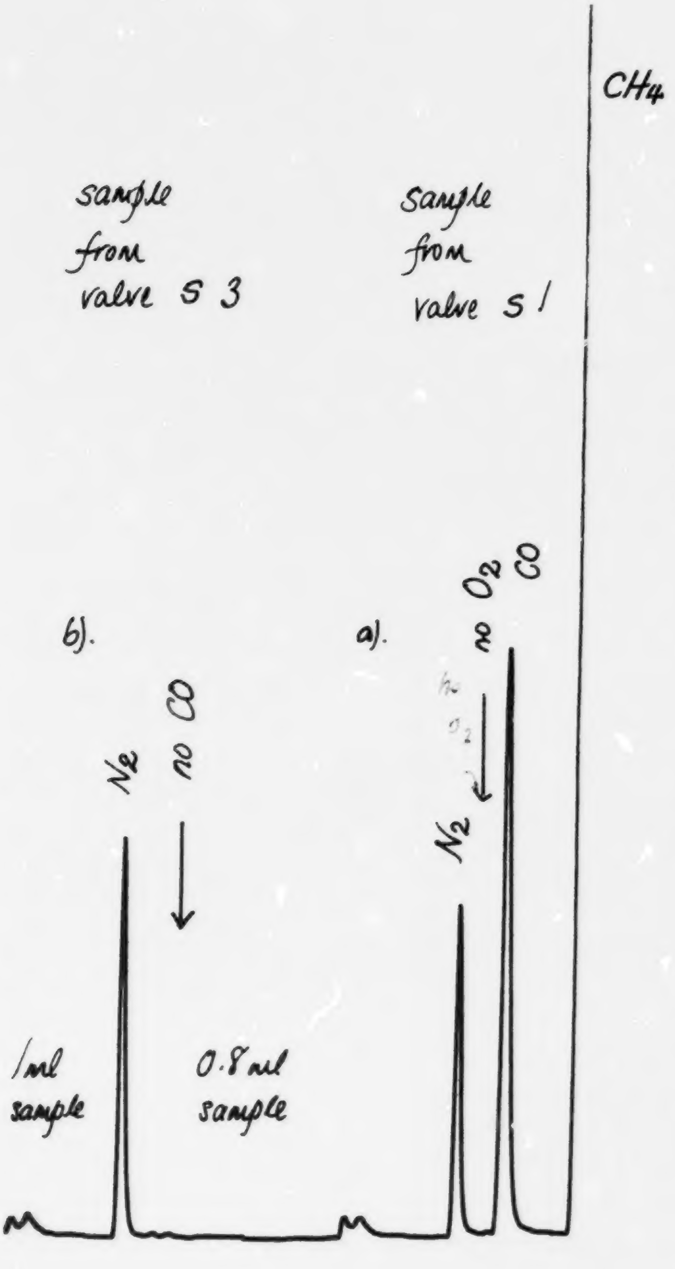


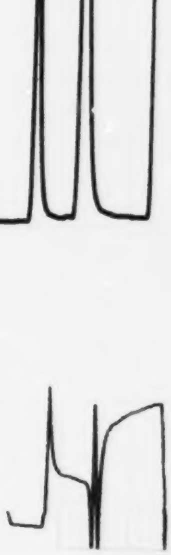
Figure 15 (iii) Recirculation III

a) Analysis of reactants for O_2.

b) Analysis of Recycle Gas for CO.

(4 hours 30 mins after admission of Reaction products to Recycle System).

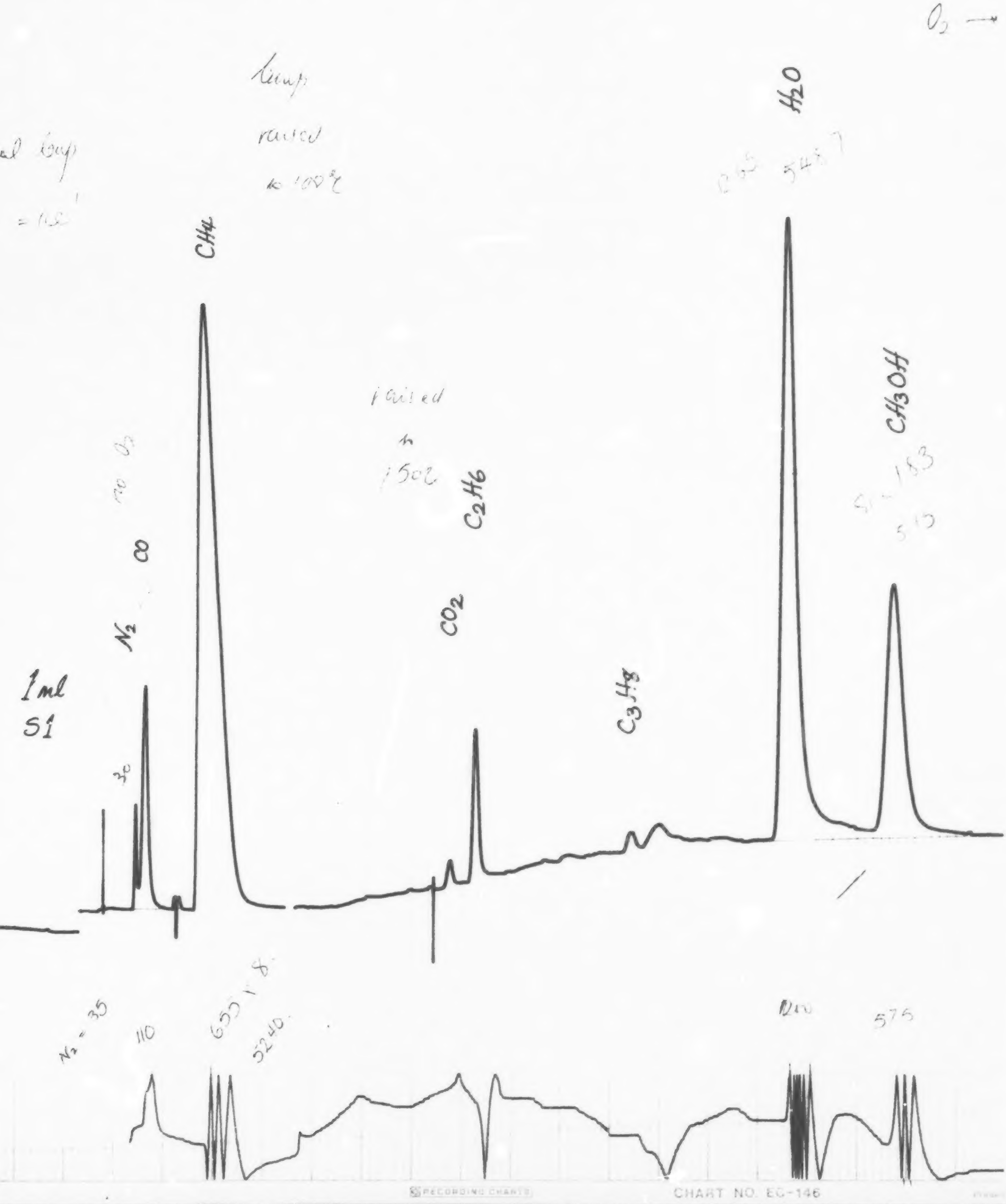




X1/6 X125 X1/6

7.

Figure 15 (iii) Recirculation III.
Analysis of reaction products
after 24 hours Recirculation.



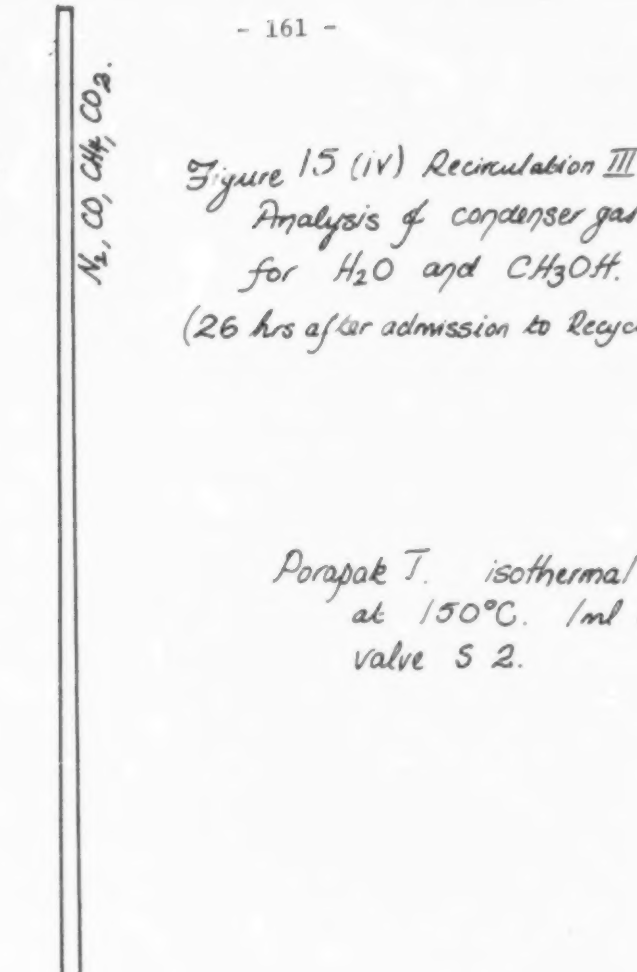
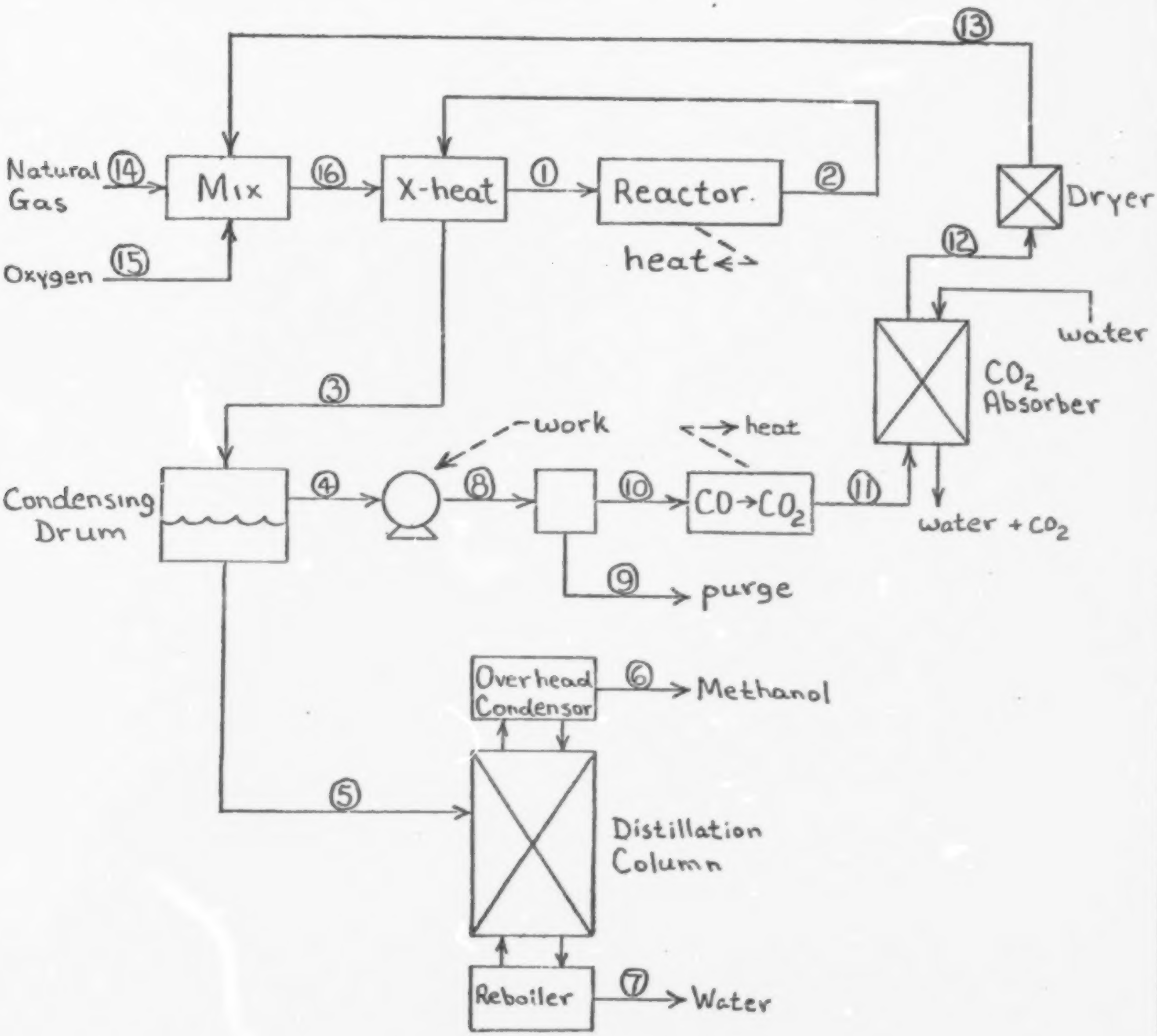


Figure 15 (iv) Recirculation III.
Analysis of condenser gas (-70°C)
for H_2O and CH_3OH.
(26 hrs after admission to Recycle system)

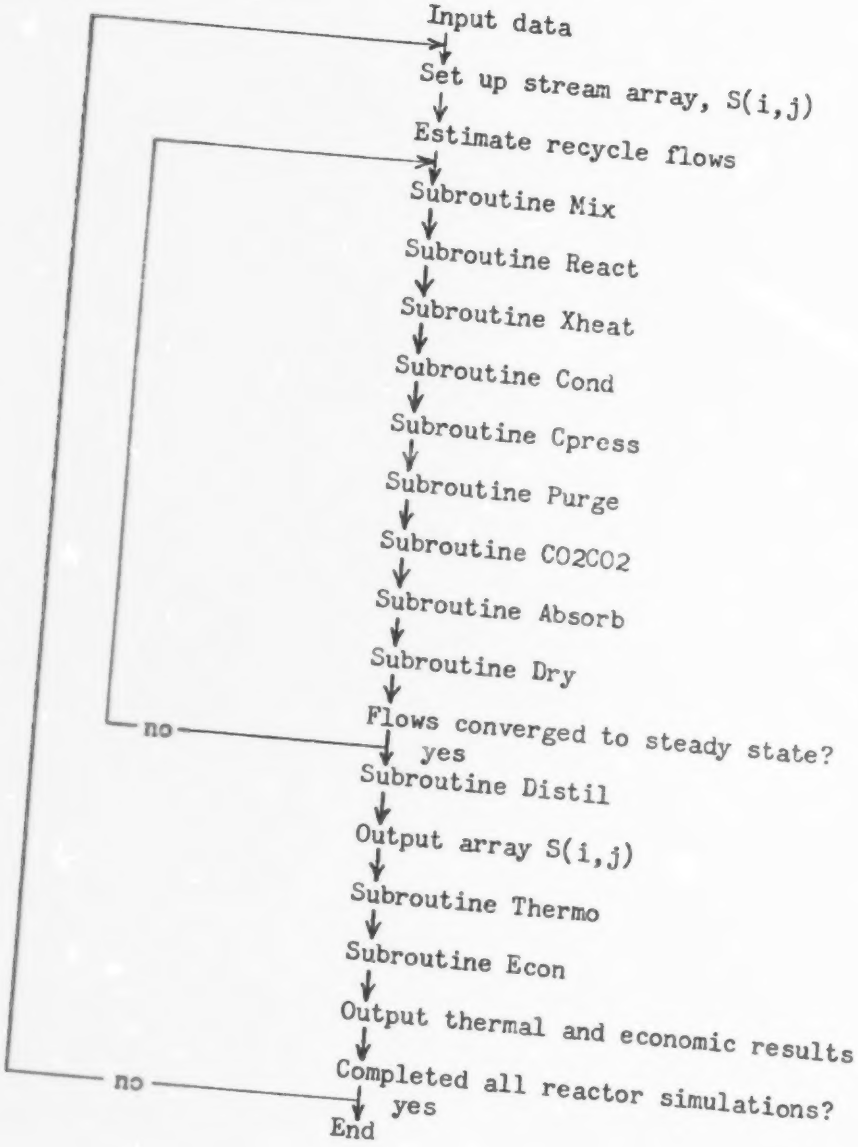
Porapak T. isothermal analysis
at 150°C. 1ml sample from
valve S 2.

Figure 16 Process Flowsheet


Natural Gas
⑭
Oxygen
⑮
Mix
⑯
X-heat
①
Reactor
②
heat
⑬
Dryer
⑫
water
CO₂ Absorber
③
Condensing Drum
④
work
⑧
⑩
heat
CO→CO₂
⑪
water + CO₂
⑨
purge
Overhead Condensor
⑥
Methanol
⑤
Distillation Column
Reboiler
⑦
Water

ⓘ denotes stream number.

Figure 17 Logic Flow


Input data
Set up stream array, S(i,j)
Estimate recycle flows
Subroutine Mix
Subroutine React
Subroutine Xheat
Subroutine Cond
Subroutine Cpress
Subroutine Purge
Subroutine CO2CO2
Subroutine Absorb
Subroutine Dry
Flows converged to steady state?
no
yes
Subroutine Distil
Output array S(i,j)
Subroutine Thermo
Subroutine Econ
Output thermal and economic results
Completed all reactor simulations?
no
yes
End